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COMPUTATIONAL METHODS FOR CALCULATION OF RATES OF EVAPORATION IN THE Ta-Hf-C SYSTEM

by Larry Kaufman and Gerald Stepakoff

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OF EVAPORATION IN THE Ta-Hf-C SYSTEM

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LIST OF FIGURES

TABLE OF CONTENTS

I. INTRODUCTION

In recent studies of phase equilibria in refractory compound systems at ManLabs, explicit methods have been developed for predicting the vapor pressures of the individual component elements over NaCl type metal carbides.[1, 2] These methods have been developed and applied to a series of refractory binary compounds which are stable over a wide range of temperature and composition. Comparison of the predicted vapor pressures with experimental measurements of congruent vaporization in HfC and ZrC yields excellent results. In addition, comparison of predicted congruently vaporizing composition in the niobium-carbon system and the observed congruency agree quite well.

On the basis of this experience, it seems worth while to extend the method, derived for binary systems, to a ternary metal-metal-carbide compound (Ta-Hf)C, which as the same stoichiometry and crystal structure as the binary carbides discussed earlier.

Under these circumstances, a theoretical study of (Ta-Hf)C was undertaken . The objectives of the present study were to

a) Apply the Schottky-Wagner model, used previously to describe binary compounds, to the ternary (Ta-Hf)C in order to generate equations capable of predicting the vapor pressures of tantalum, hafnium, and carbon over (Ta-Hf)C as a function of temperature and composition.

b) Relate the computed vapor pressure curves to rates of vaporization characteristic of specific compositions through the Langmiur equation.

c) Present explicit equations for the vapor pressure and rate of vaporization of each component as a function of temperature and composition.

and

d) Carry out explicit numerical evaluation of the vapor pressure and rate of evaporation of each component at $2200^{\circ}K$, $2600^{\circ}K$, $2800^{\circ}K$ and $3000^{\circ}K$ and at carbon levels of 41%, 46%, 49% and 50% respectively for comparison with experimentally observed results.

Subsequent portions of this report detail the methods used to accomplish the objectives described above.

II. EXTENSION OF THE SCHOTTKY-WAGNER MODEL TO TERNARY COMPOUNDS

In order to extend the treatment of Kaufman and Clougherty,[1] performed for binary compounds, to the ternary case, we consider a system A-B-C containing a ternary compound having the σ crystal structure. The composition is specified by setting (1-x-y) equal to the atom fraction of A, x equal to the atom fraction of B, and y equal to the atom fraction of C. We consider a case where two sublattices exist, the A and B atoms occupying one sublattice, while the C atoms occupy the other (i.e. A = Ta, B = Hf, C = carbon). If stoichiometry corresponds to $y = y_o$ and the total number of sites, filled and unfilled, is N_s then,

$$N_{sA} = \text{Number of A sites} = (1-x-y)(1-y_o)(1-y)^{-1}N_s$$

$$N_{sB} = \text{Number of B sites} = x(1-y_o)(1-y)^{-1}N_s$$

$$N_{sC} = \text{Number of C sites} = y_o N_s$$

while

$$N_A = \text{Number of A atoms} = (1-x-y)N$$

$$N_B = \text{Number of B atoms} = xN$$

$$N_C = \text{Number of C atoms} = yN$$

where N is Avogardro's number.

If the ratio of A atoms on A sites, N_{A1}, to A atoms on B sites, N_{A0}, is equal to the ratio of A sites to B sites (ditto for the B atoms) then

$$N_{A0} = \text{Number of A atoms on B sites} = x(1-x-y)N(1-y)^{-1}$$

$$N_{A1} = \text{Number of A atoms on A sites} = (1-x-y)^2 N(1-y)^{-1}$$

3

and

N_{B0} = Number of B atoms on A sites = $x(1-x-y)N(1-y)^{-1}$

N_{B1} = Number of B atoms on B sites = $x^2 N(1-y)^{-1}$

In line with the standard state convention adopted earlier,[1] the free-energy per gram atom F^σ is given by equation (1)

$$F^\sigma = (1-x-y)F_A^o + xF_B^o + yF_C^o + \left(\frac{N_s}{N}\right)\Delta F^\sigma + \frac{N_{A+}}{N}F_{A+} + \frac{N_{B+}}{N}F_{B+} + \frac{N_{C+}}{N}F_{C+}$$

$$+ \frac{N_{A0}}{N}F_{A0} + \frac{N_{B0}}{N}F_{B0} - kT \ln W_p \qquad (1)$$

In Eq. 1, F_A^o, F_B^o, and F_C^o are the free energies of pure A, B, and C at the temperature in question, where

$$F_A^o[0^oK] = F_B^o[0^oK] = F_C^o[0^oK] = 0 \text{ at one atmosphere} \qquad (2)$$

is the reference state. Moreover, ΔF^σ is the free energy of formation of the ternary compound for a given value of x and y_o. The free energies of A atoms on B sites and B atoms on A sites are given by F_{A0} and F_{B0}, while F_{A+}, F_{B+}, and F_{C+} are the free energies of formation for A, B, and C vacancies. The numbers of A, B, and C vacancies, which appear in Eq. 1 are given as follows:

N_{A+} = Number of vacant A sites = $(1-x-y)(1-y_o)N_s(1-y)^{-1} - (1-x-y)N$

N_{B+} = Number of vacant B sites = $x(1-y_o)N_s(1-y)^{-1} - xN$

N_{C+} = Number of vacant C sites = $y_o N_s - yN$

The final term to be evaluated in Eq. 1 is the thermodynamic probability factor W_p which is given by,

$$W_p = \frac{N_{sC}!}{N_{C+}!\,N_C!} \cdot \frac{N_{sA}!}{N_{A+}!\,N_{A1}!\,N_{B0}!} \cdot \frac{N_{sB}!}{N_{B+}!\,N_{B1}!\,N_{A0}!} \qquad (3)$$

4

Making the appropriate substitutions for the N_s and applying Stirling's formula and substitution into Eq. (1) yields for the case $y_o = 1/2$

$$F^\sigma = (1-x-y)F_A^o + xF_B^o + yF_C^o + z(\Delta F_{AC}^\sigma + x(1-y)^{-1}(\Delta F_{BC}^\sigma - \Delta F_{AC}^\sigma))$$

$$+ (0.5z + y - 1)(1-y)^{-1}((1-x-y)F_{A+} + xF_{B+}) + (0.5z - y)F_{C+} + x(1-x-y)(1-y)^{-1}W$$

$$+ RT(-z \ln 0.5z + y \ln y + x \ln x + (1-x-y) \ln(1-x-y)$$

$$+ (0.5z - y) \ln(0.5z - y) + (0.5z + y - 1) \ln(0.5z + y - 1)) \tag{4}$$

where z = ratio of sites to atoms = N_s/N, $W = F_{A0} + F_{B0}$, and the free energy of formation of the ternary compound $\Delta F^\sigma[x, y_o]$ has been approximated by a linear combination of the free energies of formation of stoichiometric AC and BC which represent TaC and HfC. Under these conditions Eq. (4) reduces to

$$F^\sigma = (1-x)F_A^o + xF_B^o + 2(\Delta F_{AC}^\sigma + x(\Delta F_{BC}^\sigma - \Delta F_{AC}^\sigma) + \frac{1}{2}F_{C+}) + Wx(1-x)$$

$$+ RT(x \ln x + (1-x) \ln(1-x)) \tag{5}$$

for the case where $y = 0$ and $N_s/N = 2$ which corresponds to a substitutional solid solution of A in B with the C sublattice empty. Eq. (5) is recognizable as being the regular solution approximation for substitutional solid solutions. In the other limits where $x = 0$ or $1-x-y = 0$ (i.e. no B or A atoms are present), Eq. (5) reduces to the equation for the binary compound identical with the expression derived earlier.[1]

The next step in the derivation is to fix the composition and minimize the free energy at constant temperature and pressure by letting the volume (i.e. the total number of sites) vary. This procedure is performed by setting the derivative of F^σ (Eq. 4) with respect to z at constant x, y, and T equal to 0.

The result is

$$2(\Delta F_{AC}^{\sigma} + x(1-y)^{-1} (\Delta F_{BC}^{\sigma} - \Delta F_{AC}^{\sigma})) + (F_{A+} + x(1-y)^{-1}(F_{B+} - F_{A+})) + F_{C+}$$
$$= -2RT \ln 2\alpha \qquad (6)$$

where

$$-2RT \ln 2\alpha = RT \ln (0.5z)^2 (0.5z-y)^{-1} (0.5z + y-1)^{-1} \qquad (7)$$

when $y = y_o = 1/2$, $\alpha = (z-1)/2z = 0.5(N_s - N)/N_s$. Thus, as in the binary case, α is the fractional number of vacant sites at stoichiometry. Substitution of Eqs. 6 and 7 into Eq. (5), i.e. minimization of the free energy with respect to volume, at constant composition, temperature, and pressure, yields

$$F^{\sigma} = (1-x-y)(F_A^o - F_{A+}) + x(F_B^o - F_{B+}) + y(F_C^o - F_{C+}) + x(1-x-y)(1-y)^{-1}W$$
$$+RT(x \ln x + y \ln y + (1-x-y) \ln (1-x-y) - y \ln (0.5z-y)$$
$$-(1-y) \ln (0.5z + y-1)) \qquad (8)$$

Eqs. 6, 7 and 8 completely define the temperature and compositional dependence of the free energy in terms of the parameters F_{A+}, F_{B+}, F_{C+}, α and W.

For the case of carbide type σ phase (NaCl type where the phase boundary on the carbon rich side approaches 50% carbon, i.e. $y_o = 1/2$,) we can approximate[1]

$$F_{C+} = -RT \ln 2\alpha = -2\Delta H^{\sigma}[0^o K] - RT \ln 2 \qquad (9)$$

where

$$2\Delta H^{\sigma}[0^o K] = 2\Delta H_{AC}^{\sigma}[0^o K] + x(1-y)^{-1}(2\Delta H_{BC}^{\sigma} - 2\Delta H_{AC}^{\sigma}) \qquad (10)$$

$$F_{A+} = -2\Delta H_{AC}^{\sigma}[0^o K] - RT \ln 2 - 2\Delta F_{AC}^{\sigma}[T] \qquad (11)$$

and

$$F_{B+} = -2\Delta H_{BC}^{\sigma}[0^o K] - RT \ln 2 - 2\Delta F_{BC}^{\sigma}[T) \qquad (12)$$

Thus in cases where the free energies of formation of the compounds AC and BC are known, at stoichiometry, as a funtion of temperature, all the parameters required are specified with the exception of W.

The final step in the present analysis is the derivation of the partial molar free energies. For the case of a binary system (i.e. if y were equal to zero) these relations are well known.

$$\overline{F}_A = F - x \frac{\partial F}{\partial x} \tag{13}$$

and

$$\overline{F}_B = F + (1-x) \frac{\partial F}{\partial x} \tag{14}$$

where $\overline{F}_A$ and $\overline{F}_B$ are the partial molar free energies of A and B and x is the atom fraction of B and (1-x) is the atom fraction of A. The analogous expressions for the ternary case are

$$\overline{F}_A = F - x\left(\frac{\partial F}{\partial x}\right)_y - y\left(\frac{\partial F}{\partial y}\right)_x \tag{15}$$

$$\overline{F}_B = F + (1-x)\left(\frac{\partial F}{\partial x}\right)_y - y\left(\frac{\partial F}{\partial y}\right)_x \tag{16}$$

$$\overline{F}_C = F - x\left(\frac{\partial F}{\partial x}\right)_y + (1-y)\left(\frac{\partial F}{\partial y}\right)_x \tag{17}$$

Since Eqs., 6, 7, and 8 yield

$$\left(\frac{\partial F}{\partial x}\right)_y = -(F_A^{\,o} - F_{A+}) + (F_B^{\,o} - F_{B+}) + W(1-2x-y)(1-y)^{-1} + RT \ln x(1-x-y)^{-1}$$
$$+ 0.5z(1-y)^{-1} \{F_{B+} - F_{A+} + 2(\Delta F_{BC}^{\sigma} - \Delta F_{AC}^{\sigma})\} \tag{18}$$

and

$$\left(\frac{\partial F}{\partial y}\right)_x = -(F_A^{\,o} - F_{A+}) + (F_C^{\,o} - F_{C+}) - W x^2(1-y)^{-2} + 0.5zx(1-y)^{-2}\{F_{B+} - F_{A+}$$
$$+ 2(\Delta F_{BC}^{\sigma} - \Delta F_{AC}^{\sigma})\} + RT \ln y(0.5z + y - 1)(1-x-y)^{-1}(0.5z-y)^{-1} \tag{19}$$

Substitution into Eqs., 15, 16, and 17 yields the expression for the partial molar free energies as follows:

$$\overline{F}_A^\sigma - F_A^o = -F_{A+} + W x^2 (1-y)^{-2} - 0.5xz (1-y)^{-2} (F_{B+} - F_{A+} + 2(\Delta F_{BC}^\sigma - \Delta F_{AC}^\sigma))$$

$$+ RT \ln (1-x-y) (0.5z + y-1)^{-1} \tag{20}$$

$$\overline{F}_B^\sigma - F_B^o = -F_{B+} + W(1-x-y)^2 (1-y)^{-2} + 0.5(1-x-y) z (1-y)^{-2}(F_{B+} - F_{A+}$$

$$+ 2(\Delta F_{BC}^\sigma - \Delta F_{AC}^\sigma)) + RT \ln x (0.5z + y-1)^{-1} \tag{21}$$

$$\overline{F}_C^\sigma - F_C^o = -F_{C+} + RT \ln y (0.5z - y)^{-1} \tag{22}$$

Since

$$\overline{F}_A^\sigma - F_A^o = RT \ln p_A^\sigma [x, y] / p_A^o \tag{23}$$

$$\overline{F}_B^\sigma - F_B^o = RT \ln p_B^\sigma [x, y] / p_B^o \tag{24}$$

and

$$\overline{F}_C^\sigma - F_C^o = RT \ln p_C^\sigma [x, y] / p_C^o \tag{25}$$

where $p_A^\sigma[x, y]$, $p_B^\sigma[x, y]$, and $p_C^\sigma[x, y]$ are the pressures of A, B, and C respectively over the alloys and p_A^o, p_B^o, and p_C^o are the corresponding vapor pressures of the pure elements, Eqs. 20 through 25 can be used to compute the vapor pressures of the elements over the alloys.

In particular when $y = y_o = 0.5$

$$\overline{F}_A^\sigma - F_A^o = -F_{A+} + 4Wx^2 - 2x(F_{B+} - F_{A+} + 2(\Delta F_{BC}^\sigma - \Delta F_{AC}^\sigma))$$

$$+ RT \ln (0.5 - x) (1 - 2\alpha) \alpha^{-1} \tag{26}$$

$$\overline{F}_B^\sigma - F_B^o = -F_{B+} + 4W(0.5-x)^2 + 2(0.5-x)(F_{B+} - F_{A+} + 2(\Delta F_{BC}^\sigma - \Delta F_{AC}^\sigma))$$

$$+ RT \ln x(1 - 2\alpha) \alpha^{-1} \tag{27}$$

and

$$\overline{F}_C^\sigma - F_C^o = -F_{C+} + RT \ln 0.5 (1 - 2\alpha) \alpha^{-1} \tag{28}$$

where z can be approximated by unity.

8

When y is less than 0.5, $z \approx 2(1-y)$ and $(0.5z + y - 1)$ is approximately equal to $4\alpha^2(1-y)^2(1-2y)^{-1}$. Under these conditions Eqs. 19 through 21 reduce to

$$\overline{F}_A^{\sigma} - F_A^{\ o} = -F_{A+} + W x^2 (1-y)^{-2} - x(1-y)^{-1}(F_{B+} - F_{A+} + 2(\Delta F_{BC}^{\sigma} - \Delta F_{AC}^{\sigma}))$$

$$+ RT \ln(1-x-y)(1-2y) \, 4^{-1} \alpha^{-2}(1-y)^{-2} \tag{29}$$

$$\overline{F}_B^{\sigma} - F_B^{\ o} = -F_{B+} + W(1-x-y)^2(1-y)^{-2} + (1-x-y)(1-y)^{-1}(F_{B+} - F_{A+} + 2(\Delta F_{BC}^{\sigma} - \Delta F_{AC}^{\sigma}))$$

$$+ RT \ln x(1-2y) \, 4^{-1} \alpha^{-2}(1-y)^{-2} \tag{30}$$

and

$$\overline{F}_C^{\sigma} - F_C^{\ o} = -F_{C+} + RT \ln y(1-2y)^{-1} \tag{31}$$

When y is greater than 0.5, $z \approx 2y$, and $(0.5z - y)$ is approximately $4\alpha^2 y^2 (2y-1)^{-1}$ and

$$\overline{F}_A^{\sigma} - F_A^{\ o} = -F_{A+} + W x^2 (1-y)^{-2} - xy(1-y)^{-2}(F_{B+} - F_{A+} + 2(\Delta F_{BC}^{\sigma} - \Delta F_{AC}^{\sigma}))$$

$$+ RT \ln(1-x-y)(2y-1)^{-1} \tag{32}$$

$$\overline{F}_B^{\sigma} - F_B^{\ o} = -F_{B+} + W(1-x-y)^2(1-y)^{-2} + (1-x-y)y(1-y)^{-2}(F_{B+} - F_{A+} + 2(\Delta F_{BC}^{\sigma} - \Delta F_{AC}^{\sigma}))$$

$$+ RT \ln x(2y-1)^{-1} \tag{33}$$

$$\overline{F}_C^{\sigma} - F_C^{\ o} = -F_{C+} + RT \ln (2y-1) \, 4^{-1} \alpha^{-2} y^{-1} \tag{34}$$

As pointed out previously, these equations are completely explicit only if W is known. Consequently W can be determined from limited data or approximated by W = 0. In the latter case, Eqs. 26 through 34 can be used to compute phase equilibria, vapor pressures, rates of free evaporation, or compositions of congruent vaporization.

9

III. APPLICATION OF MODEL TO Ta - Hf -C SYSTEM

In order to apply the equations developed in Section II to the tantalum-hafnium-carbon system in explicit terms, it is necessary to assume that W = 0. Moreover since the NaCℓ type σ phase exists for values of y (atomic fraction of carbon) which are less than or equal to 0.5, Eqs. 26 through 31 can be applied. In this system, tantalum is element A, hafnium is element B, and carbon is element C. Table I contains the relevant values for the free energy of formation of stoichiometric HfC and TaC. These values are the same as the values employed in an earlier study of the binary carbides.[2] Consequently, Eqs. (26) to (28) yield the following expressions for y = 0.5.

$$RT\ell n \ p^{\sigma}_{Ta}[x] / p^{o}_{Ta+} = -F_{Ta+} -2x(23,100) - RT\ell n \ \alpha$$
$$+RT\ell n \ (0.5-x) \tag{35}$$

$$RT\ell n \ p^{\sigma}_{Hf}[x] / p^{o}_{Hf+} = -F_{Hf+} +2(0.5-x) (23,100) -RT\ell n \ \alpha$$
$$+RT\ell nx \tag{36}$$

and

$$RT\ell n \ p^{\sigma}_{C}[x] / p^{o}_{C} = -F_{C+} - RT\ell n \ 2 \ \alpha \tag{37}$$

since 1 - 2α is nearly equal to unity. On the basis of Table I and Eqs. (9) and (10)

$$RT\ell n\alpha = -35,900 - x(1 - y)^{-1} \ 23,100 \ cal/g.at. \tag{38}$$

10

Table I

Summary of Numerical Values Required For
Vapor Pressure Computations

$$2\Delta H^{\sigma}_{TaC}[\,0^{\circ}K] \approx -35,900 \text{ cal/mol}$$

$$2\Delta H^{\sigma}_{HfC}[\,0^{\circ}K] \approx -59,000 \text{ cal/mol}$$

$T^{\circ}K$	$2\Delta F^{\sigma}_{TaC}[\,T]$ cal/mol	F_{Ta+} cal/g.at.	$RT\ell n\,2$ cal/g.at.	$2\Delta F^{\sigma}_{HfC}[\,T]$ cal/mol	F^{σ}_{Hf+} cal/g.at.
2200	-33,260	+66,126	3034	-54,200	110,165
2600	-32,780	+65,095	3585	-53,100	108,515
2800	-32,540	+64,579	3861	-52,100	107,240
3000	-32,300	+64,063	4137	-51,200	106,065

source: Ref(2) pp(21) and (69)

$T^{\circ}K$	$-\log p^{o}_{C}$	$-\log p^{o}_{Ta}$	$-\log p^{o}_{Hf}$
	(pressure in units of atmospheres)		
2200	8.781	11.206	7.382
2600	6.174	8.346	5.246
2800	5.151	7.219	4.412
3000	4.266	6.243	3.692

source: C - JANAF Thermochemical Tables

Hf and Ta - S.A.R. #2 AF33(657)8635 - "Borides" p VII f-6

$$RT\ell n\alpha = -35,900 - x(1-y)^{-1}\,23,100 \quad (\text{from Eqs. (9), (10)})$$

$$F_{C+}[\,x,T] = -RT\,\ell n\,2\,\alpha \qquad (\text{from Eq. (9)})$$

$$(F_{Hf+} - F_{Ta+} + 2(\Delta F^{\sigma}_{HfC} - \Delta F^{\sigma}_{TaC})) = 23,100 \text{ cal/g.at.} \quad (\text{from Eqs. (11) and (12)})$$

When $y < 0.5$, Eqs. 29 to 31 yield

$$RT\ell n\ p^{\sigma}_{Ta}\ [x, y\ ]/p^{o}_{Ta} = -\ F_{Ta+} - x(1-y)^{-1}\ 23,100 - 2RT\ell n\ \alpha$$

$$+ RT\ell n\ (1-x-y)\ (1-2y)\ 4^{-1}\ (1-y)^{-2} \tag{39}$$

$$RT\ell n\ p^{\sigma}_{Hf}\ [x, y]\ /p^{o}_{Hf} = -\ F_{Hf+} + (1-x-y)\ (1-y)^{-1}\ 23,100 - 2RT\ell n\ \alpha$$

$$+ RT\ell n\ x\ (1-2y)\ 4^{-1}\ (1-y)^{-2} \tag{40}$$

and

$$RT\ell n\ p^{\sigma}_{C}\ [x, y]\ /p^{o}_{C} = -\ F_{C+} + RT\ell n\ y\ (1-2y)^{-1} \tag{41}$$

Eqs. 35 through 41 define the vapor pressures of tantalum, hafnium, and carbon as a function of x, y and T. Numerical calculation of these quantities has been performed for four carbon levels, $y = 0.50, 0.49, 0.46,$ and 0.41 at temperatures of $2200, 2600, 2800$ and $3000^{\circ}K$. Graphical representations of these results are shown in Figs. 1 to 16.[*] In addition, the rates of Langmuir evaporation for each component has been computed as follows:

$$\dot{\nu}_{Ta} = 44.4\ p^{\sigma}_{Ta}\ [\ x, y, T]\ (M_{Ta})^{1/2}\ T^{-1/2}\ gms/cm^{2}\ sec \tag{42}$$

$$\dot{\nu}_{Hf} = 44.4\ p^{\sigma}_{Hf}\ [x,\ y,\ T]\ (M_{Hf})^{1/2}\ T^{-1/2}\ gms/cm^{2}\ sec \tag{43}$$

$$\dot{\nu}_{C} = 44.4\ p^{\sigma}_{C}\ [x,\ y,\ T]\ (M_{C})^{1/2}\ T^{-1/2}\ gms/cm^{2}\ sec \tag{44}$$

where M_{Ta}, M_{Hf}, and M_{C} are the atomic masses of tantalum, hafnium, and carbon respectively.

[*]These temperatures and compositions were agreed upon at a meeting between L. Kaufman, of ManLabs and H.B. Probst, D. Deadmore and I. Zaplatynsky of N.A.S.A.
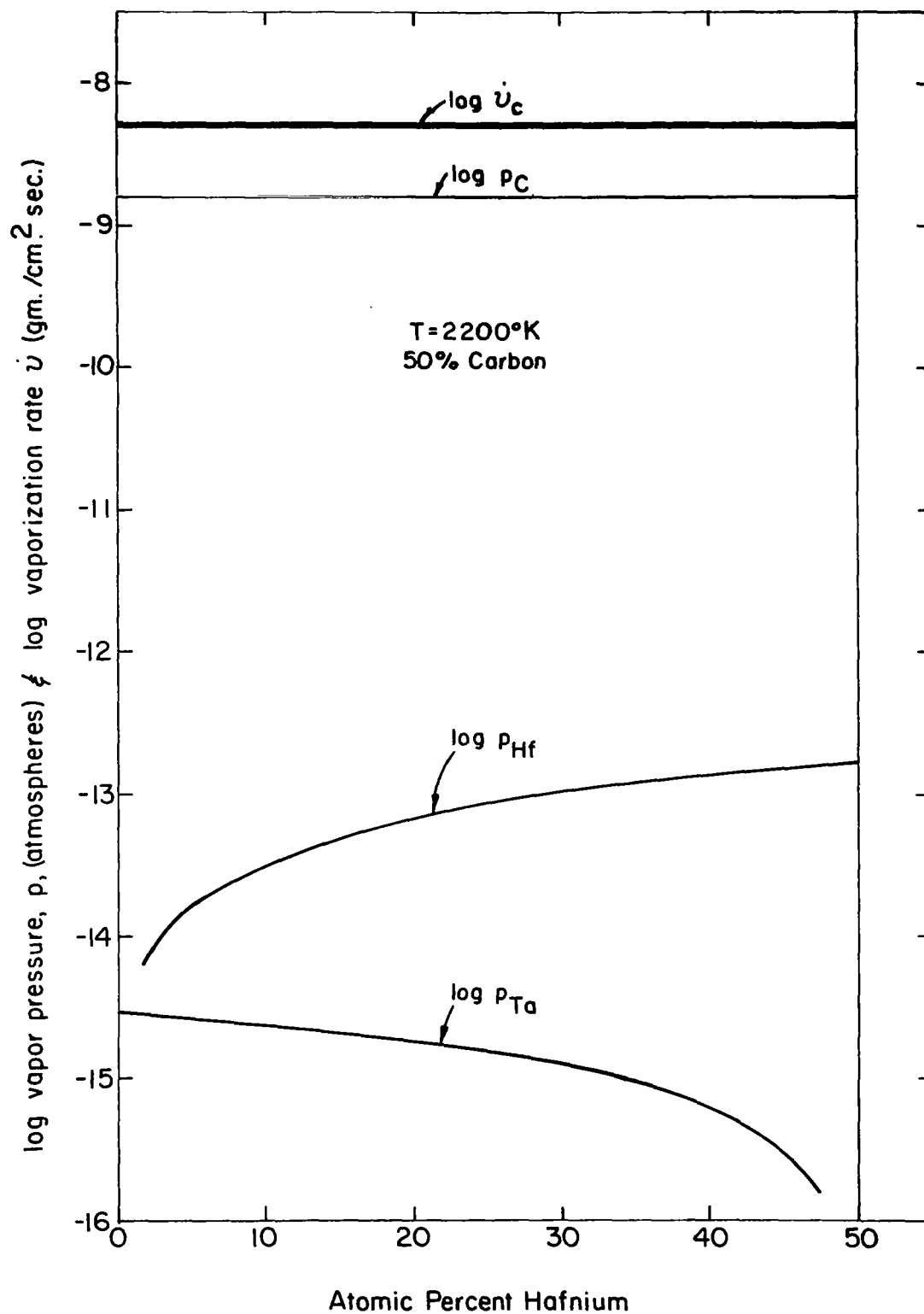
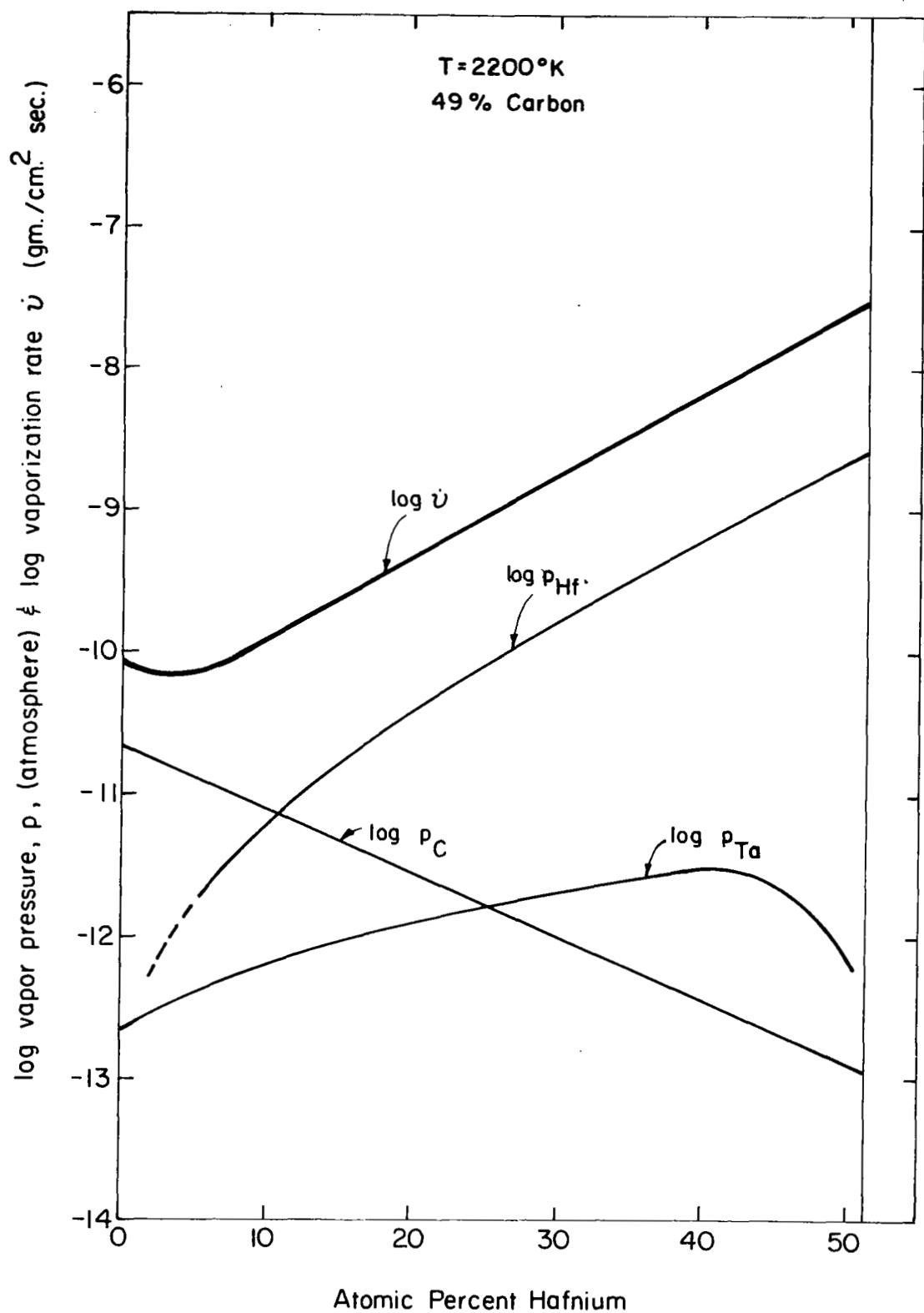**Fig. 1** - Vaporization of (Ta-Hf) C at 2200°K and 50% carbon.

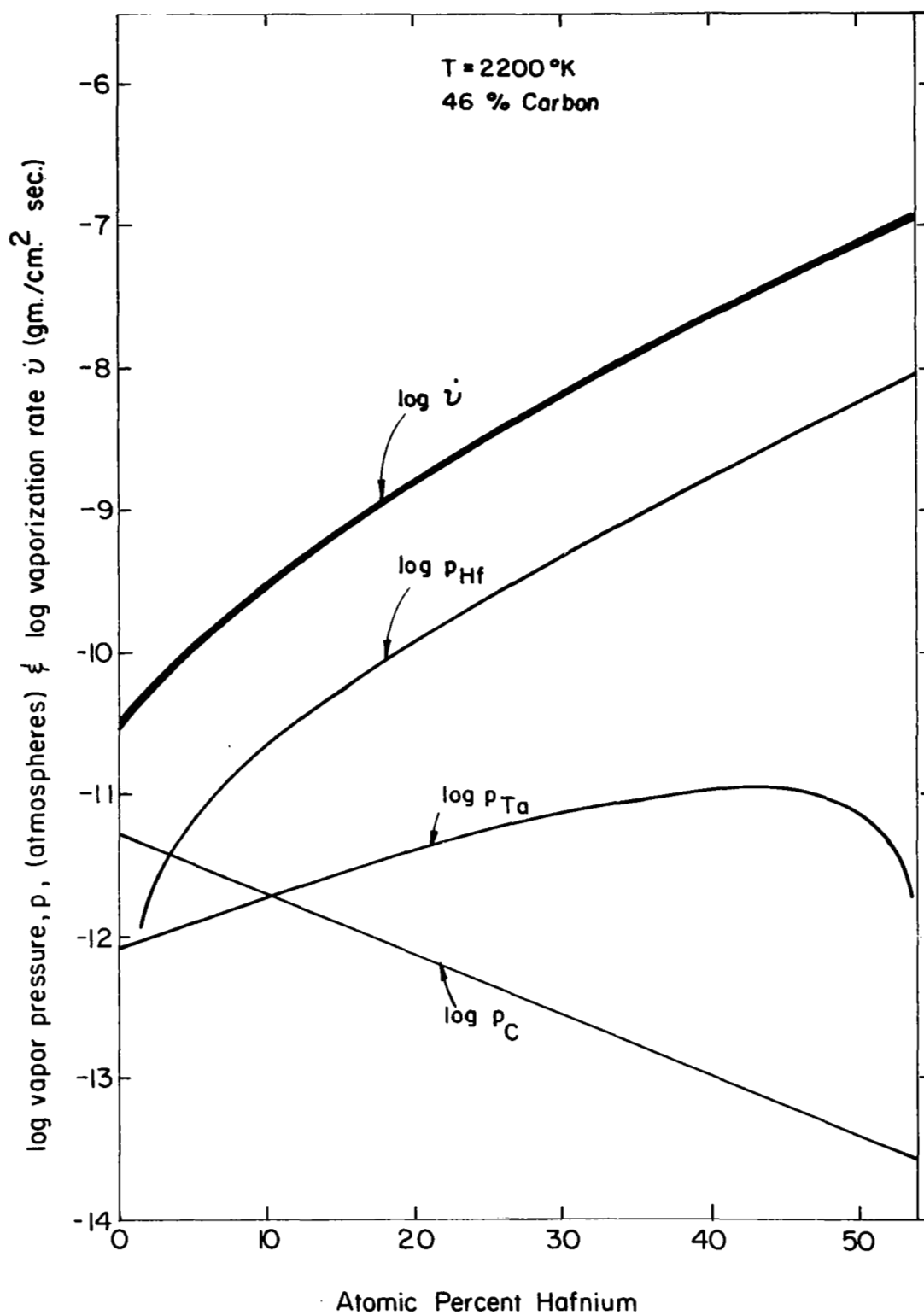**Fig. 2** - Vaporization of (Ta-Hf)C at 2200°K and 49% carbon.

14

Fig. 3 - Vaporization of (Ta-Hf)C at 2200°K and 46% carbon.
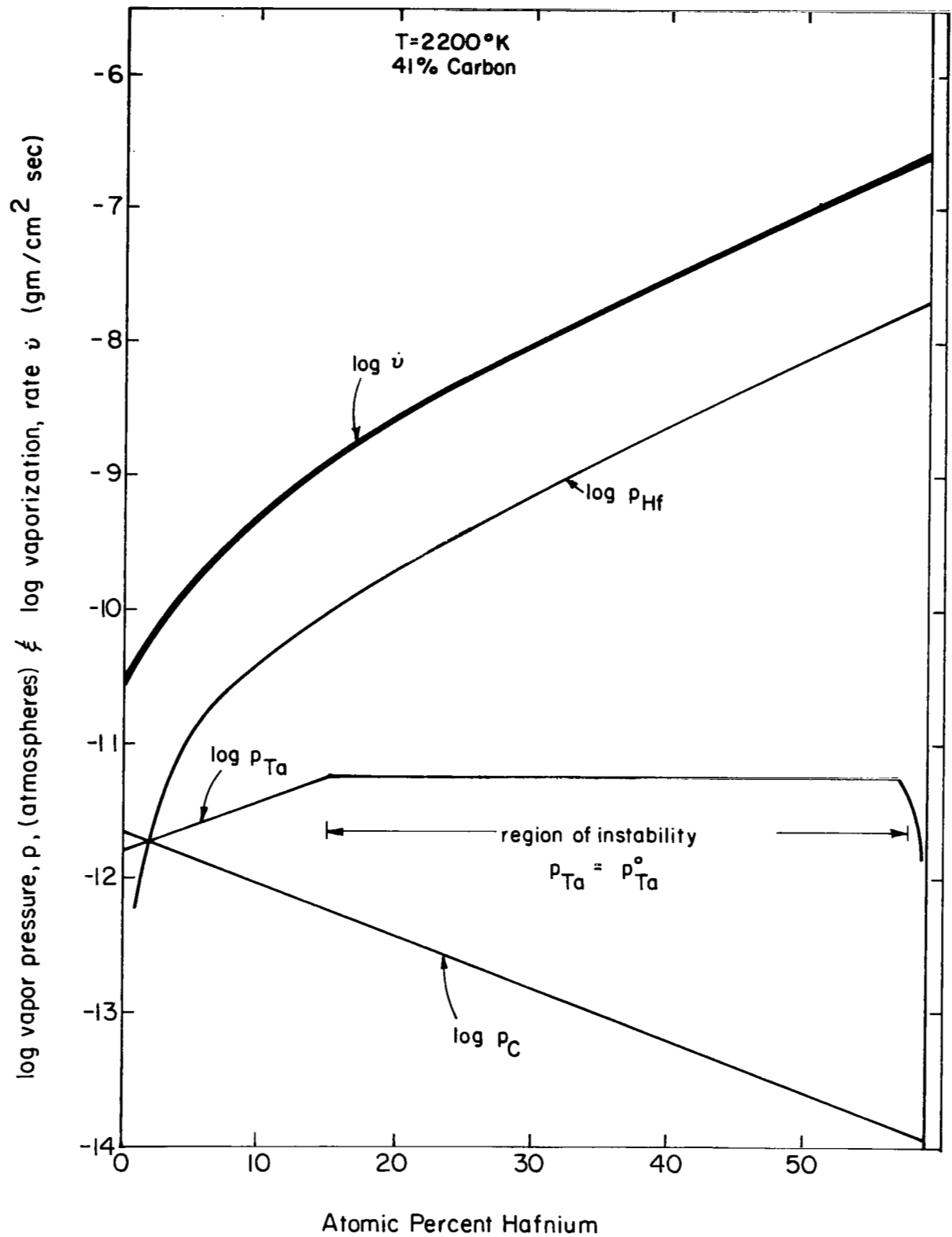
15

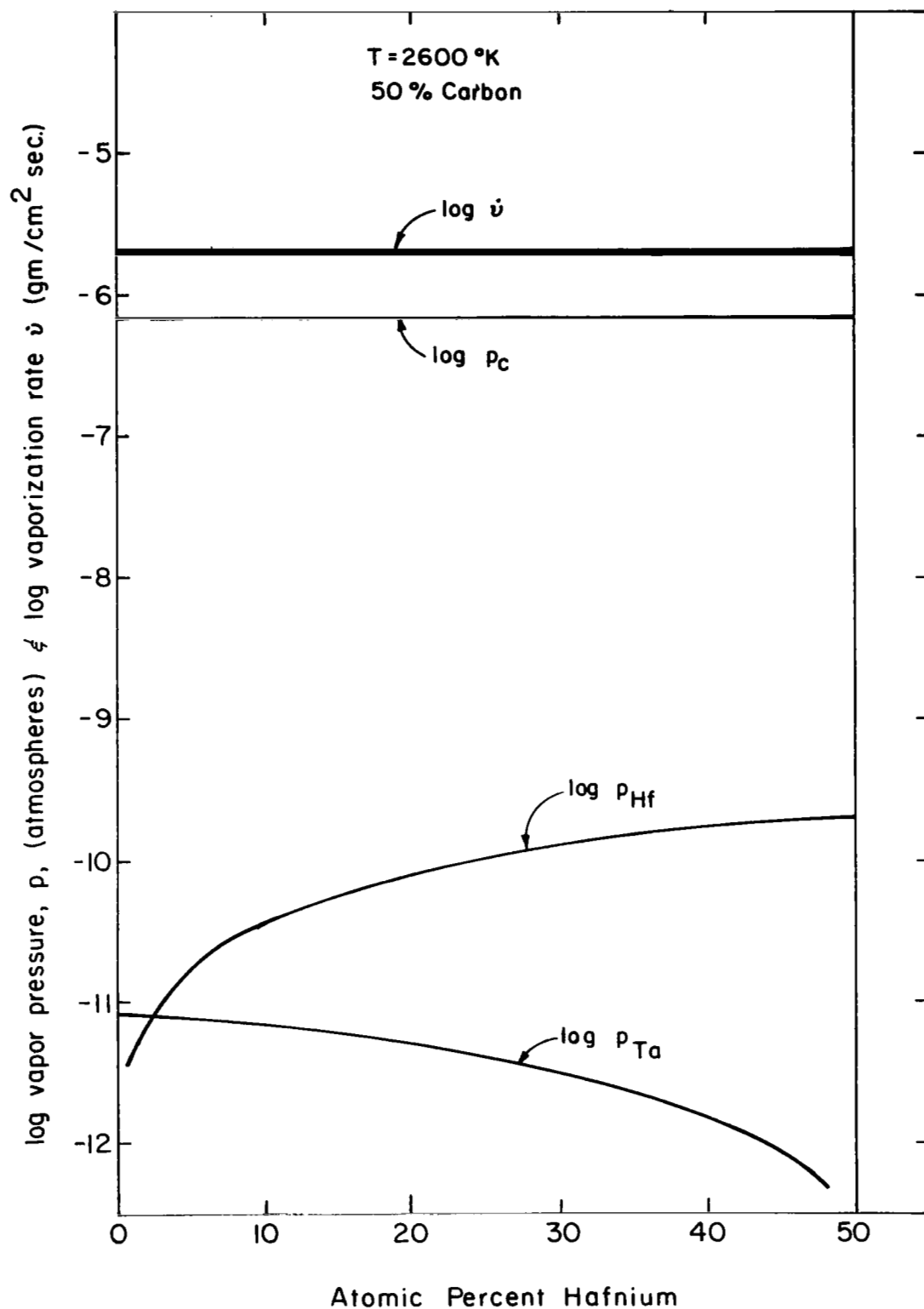Fig. 4 - Vaporization of (Ta-Hf)C at 2200°K and 41% Carbon.

16

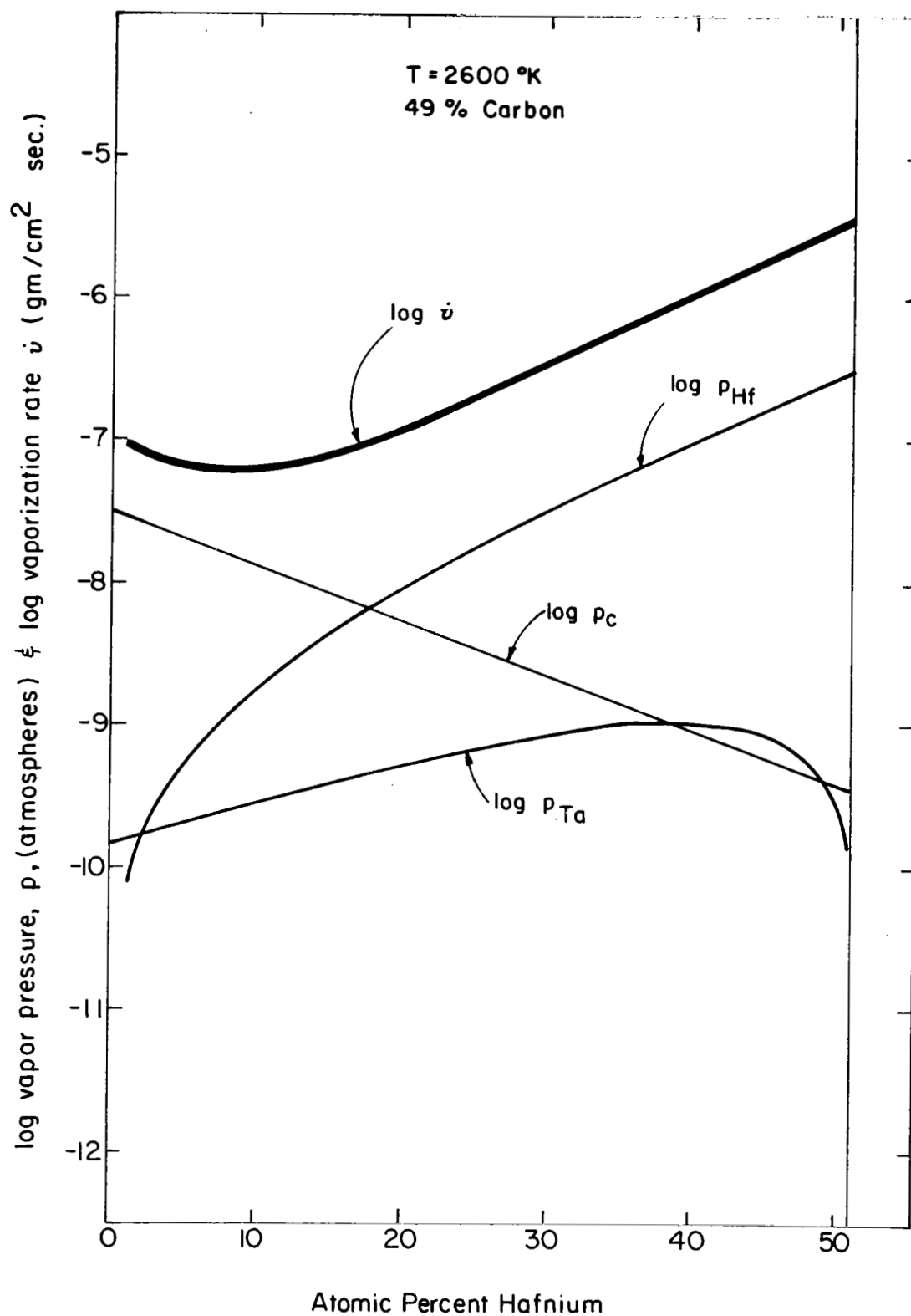Fig. 5 - Vaporization of (Ta-Hf)C at 2600°K and 50% carbo

17

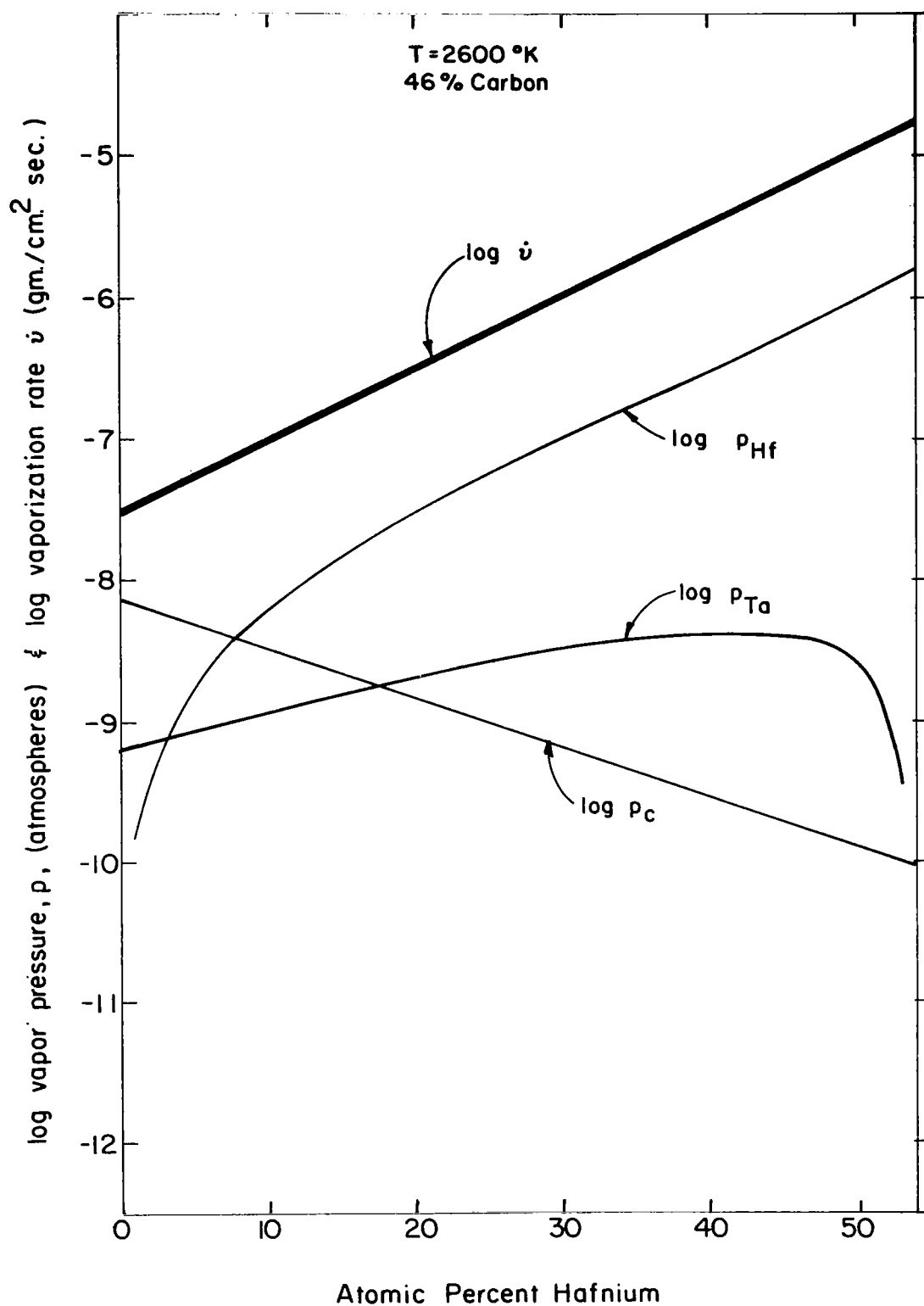Fig. 6 - Vaporization of (Ta-Hf) C at 2600°K and 49% carbon.

18

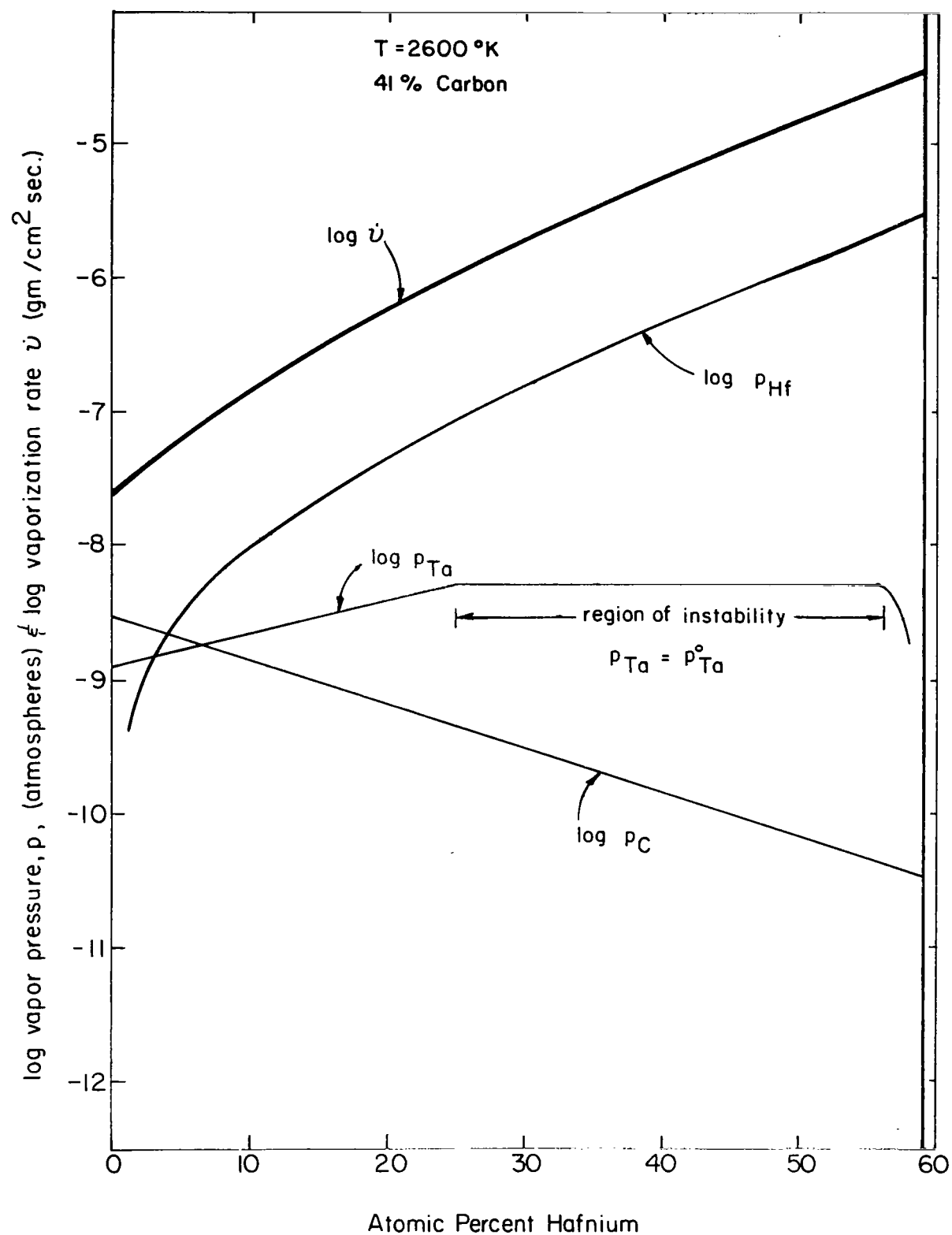Fig. 7 - Vaporization of (Ta-Hf)C at 2600°K and 46% carbon.

19

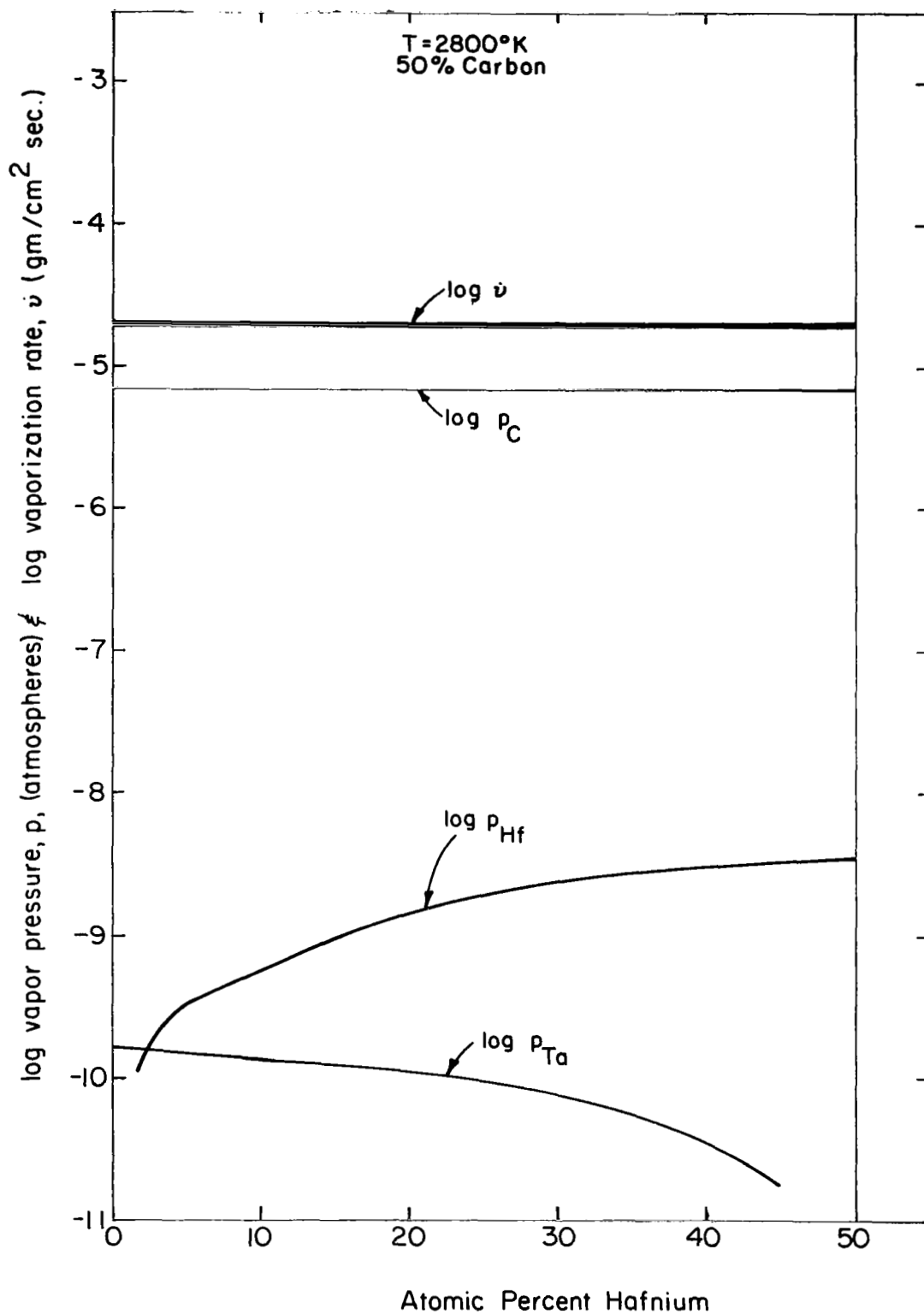Fig. 8 - Vaporization of (Ta-Hf)C at 2600°K and 41% carbon.

20

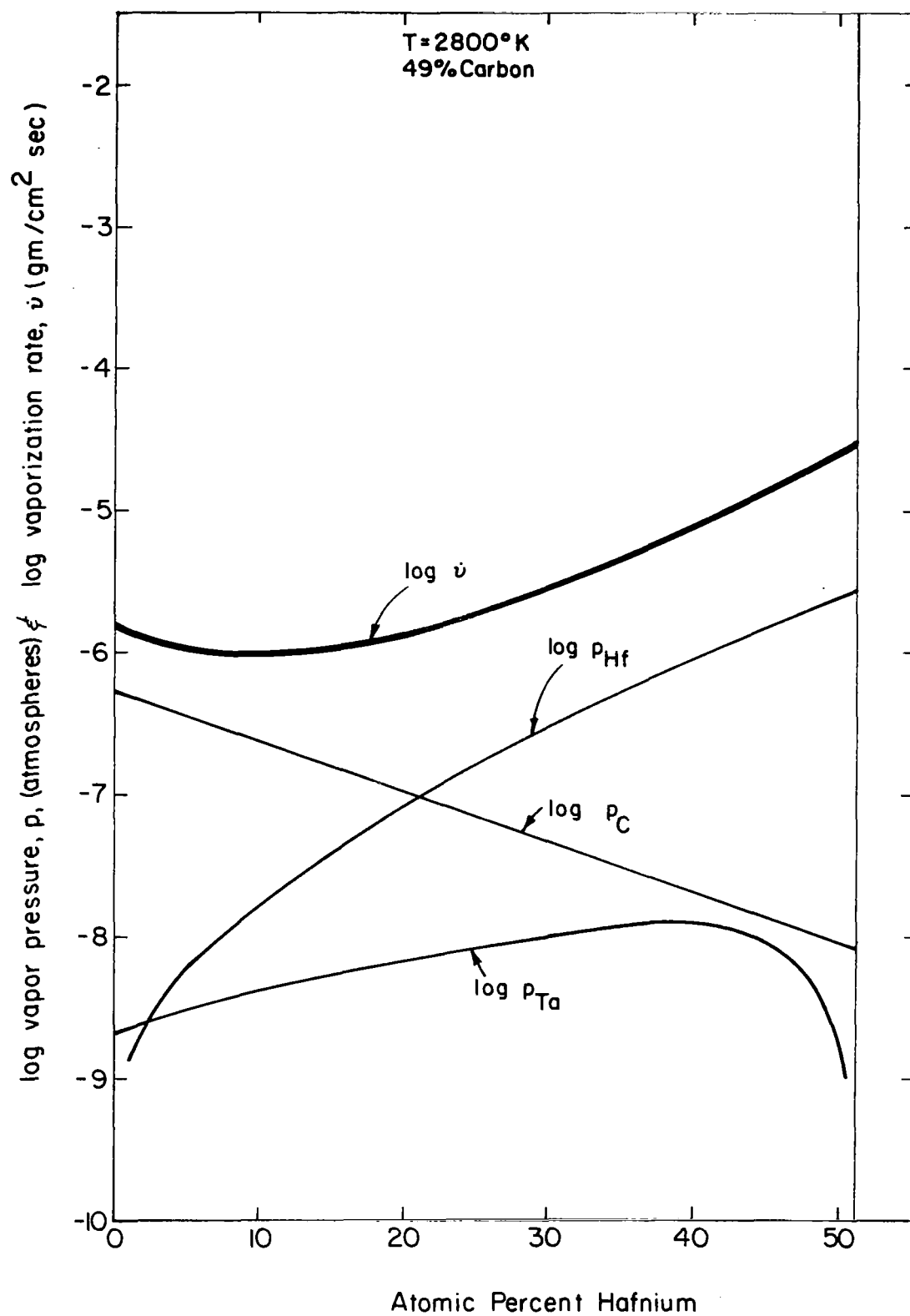Fig. 9 - Vaporization of (Ta-Hf) C at 2800°K and 50% carbon.

21

Fig. 10 - Vaporization of (Ta-Hf) C at 2800°K and 49% carbon.
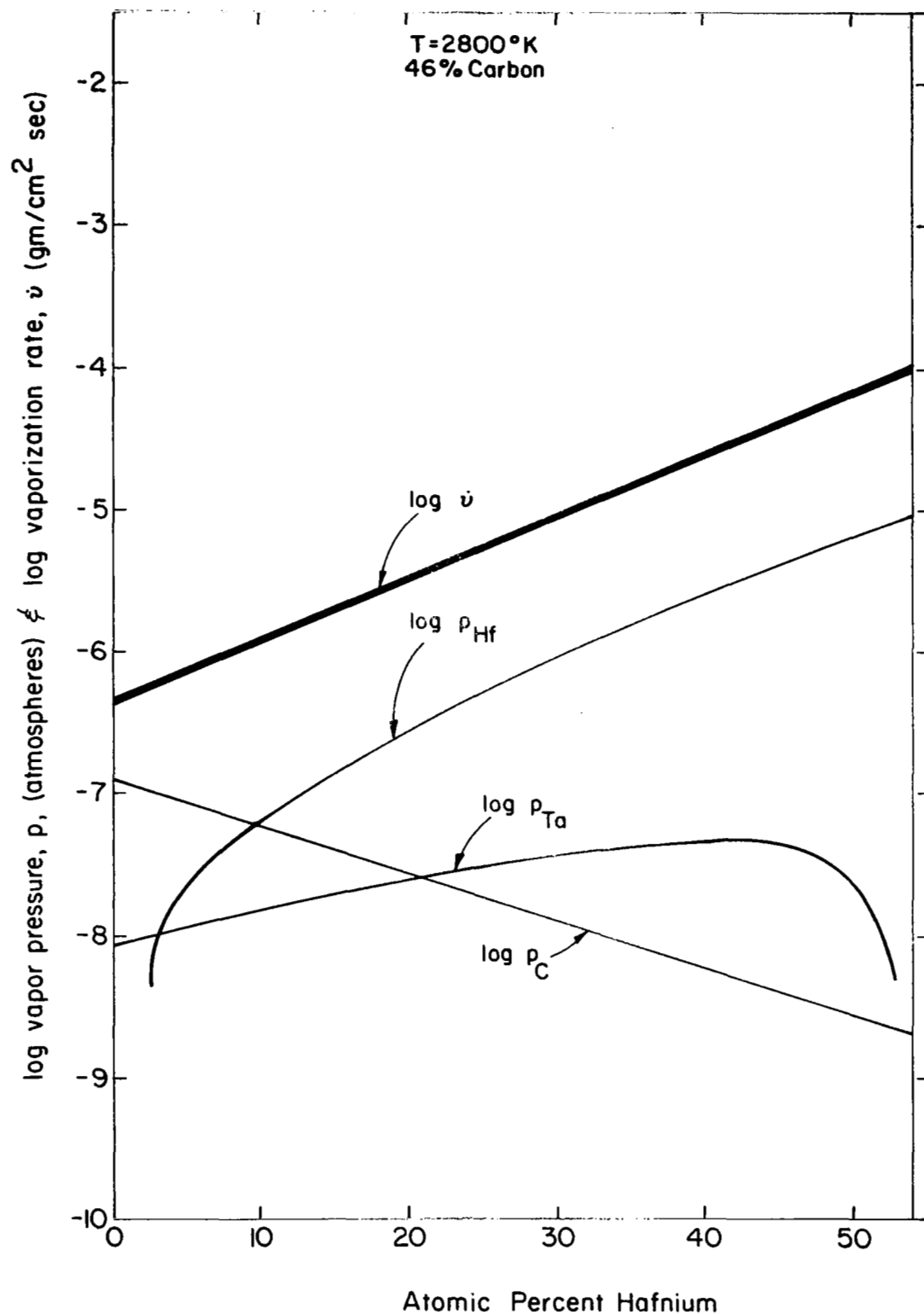
22

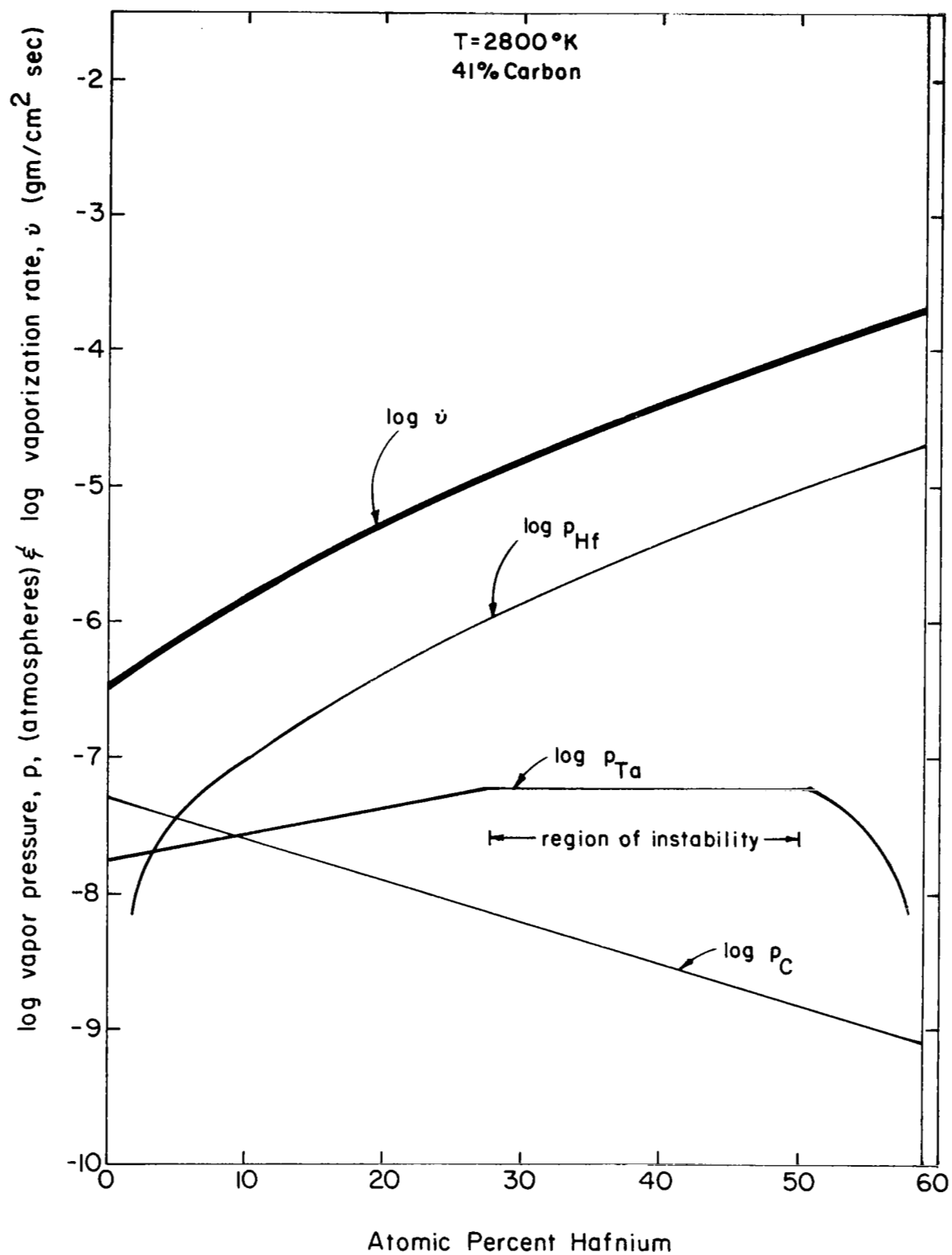**Fig. 11** - Vaporization of (Ta-Hf) C at 2800°K and 46% carbon.

23

Fig. 12-Vaporization of (Ta-Hf) C at 2800°K and 41% carbon.
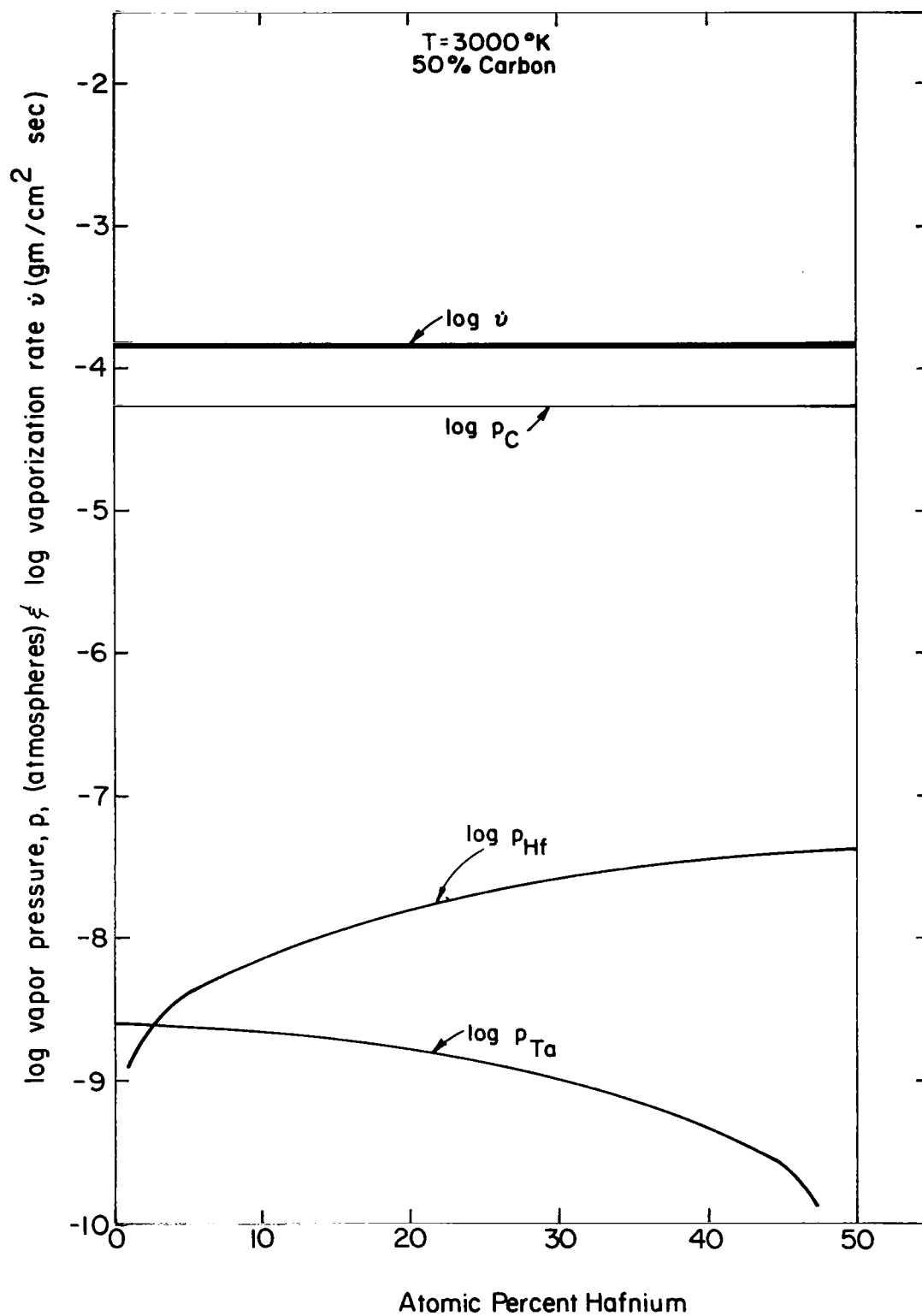
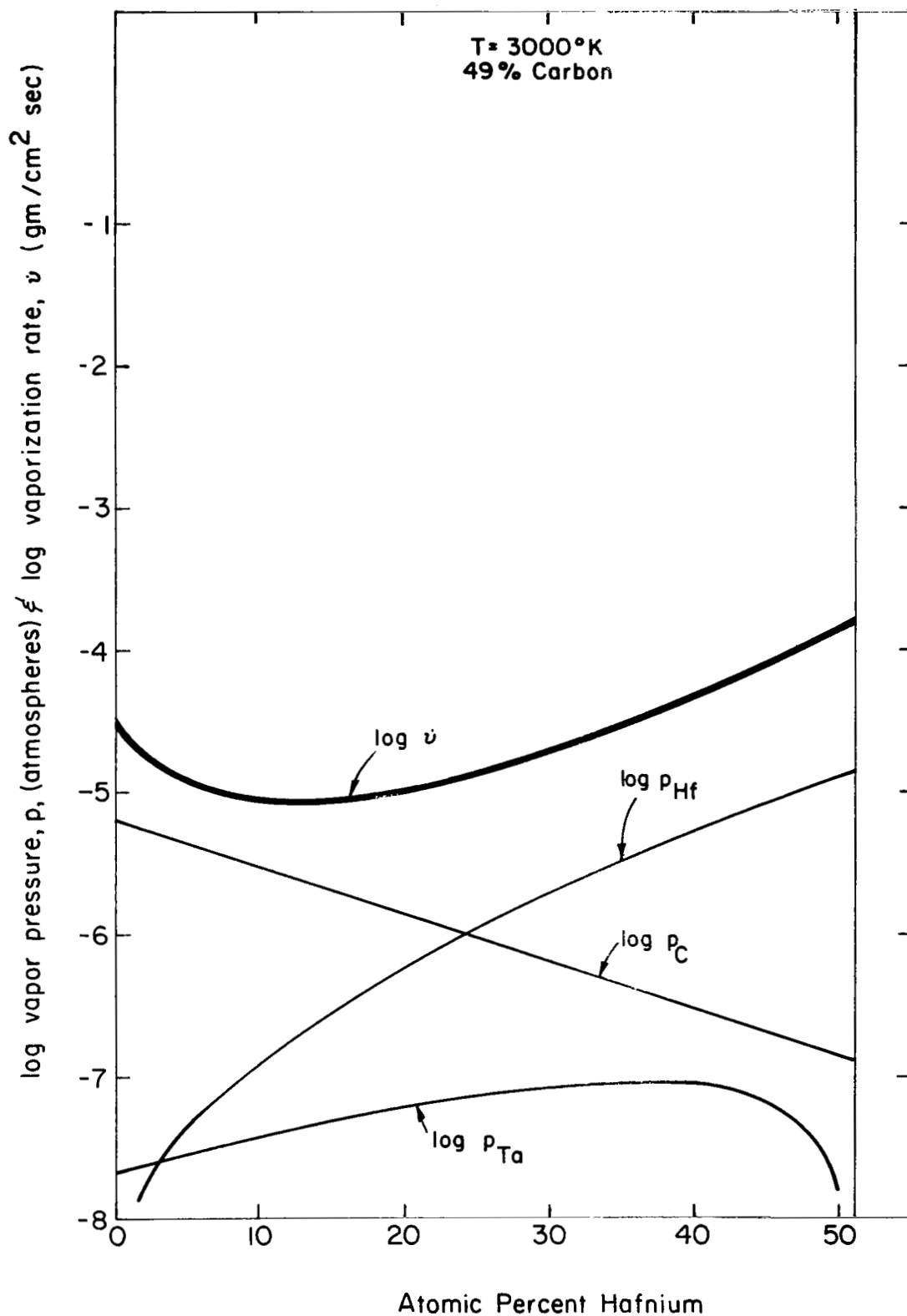**Fig. 13 -** Vaporization of (Ta-Hf)C at 3000°K and 50% carbon.

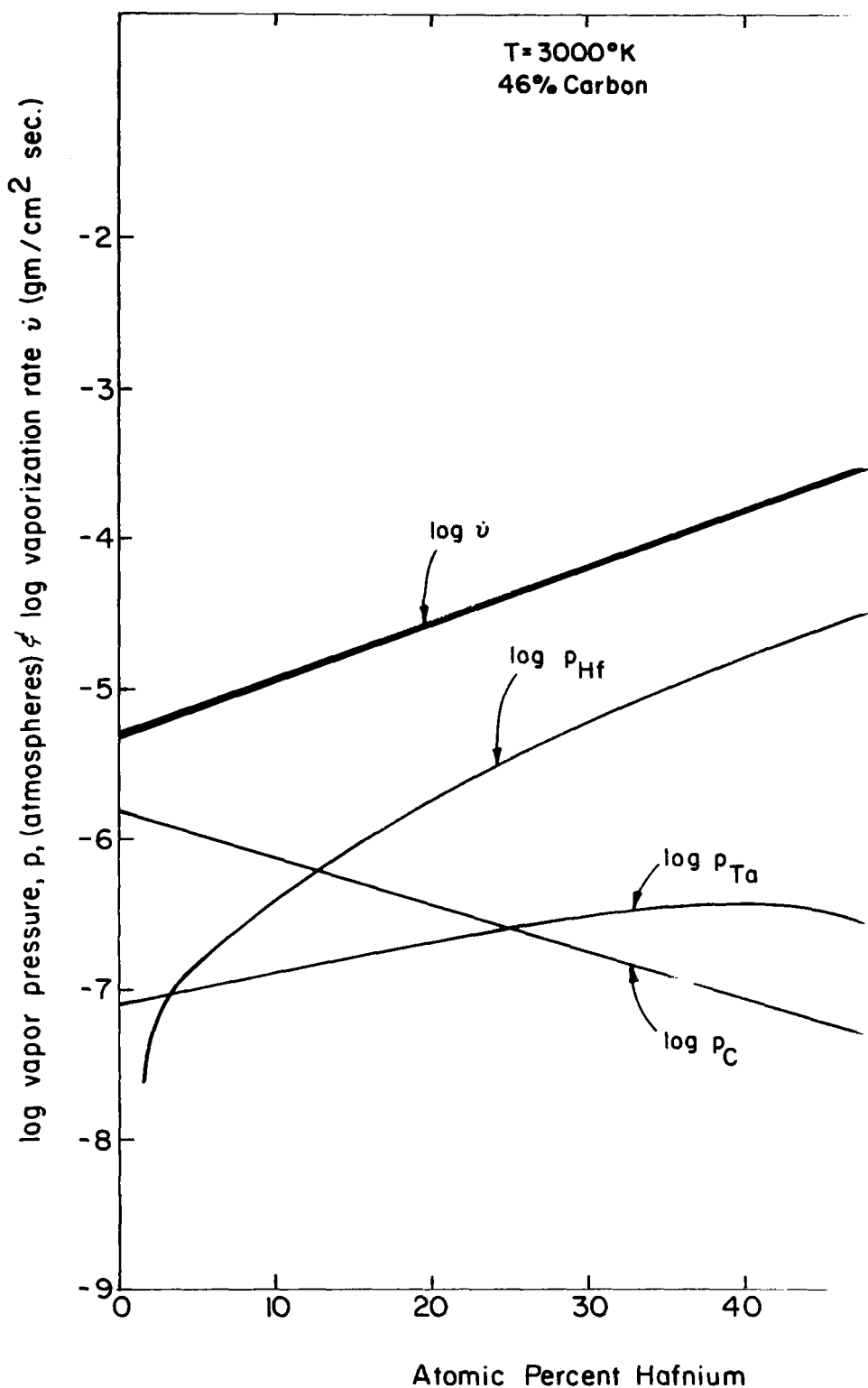Fig. 14 - Vaporization of (Ta-Hf)C at 3000°K and 49% carbon.
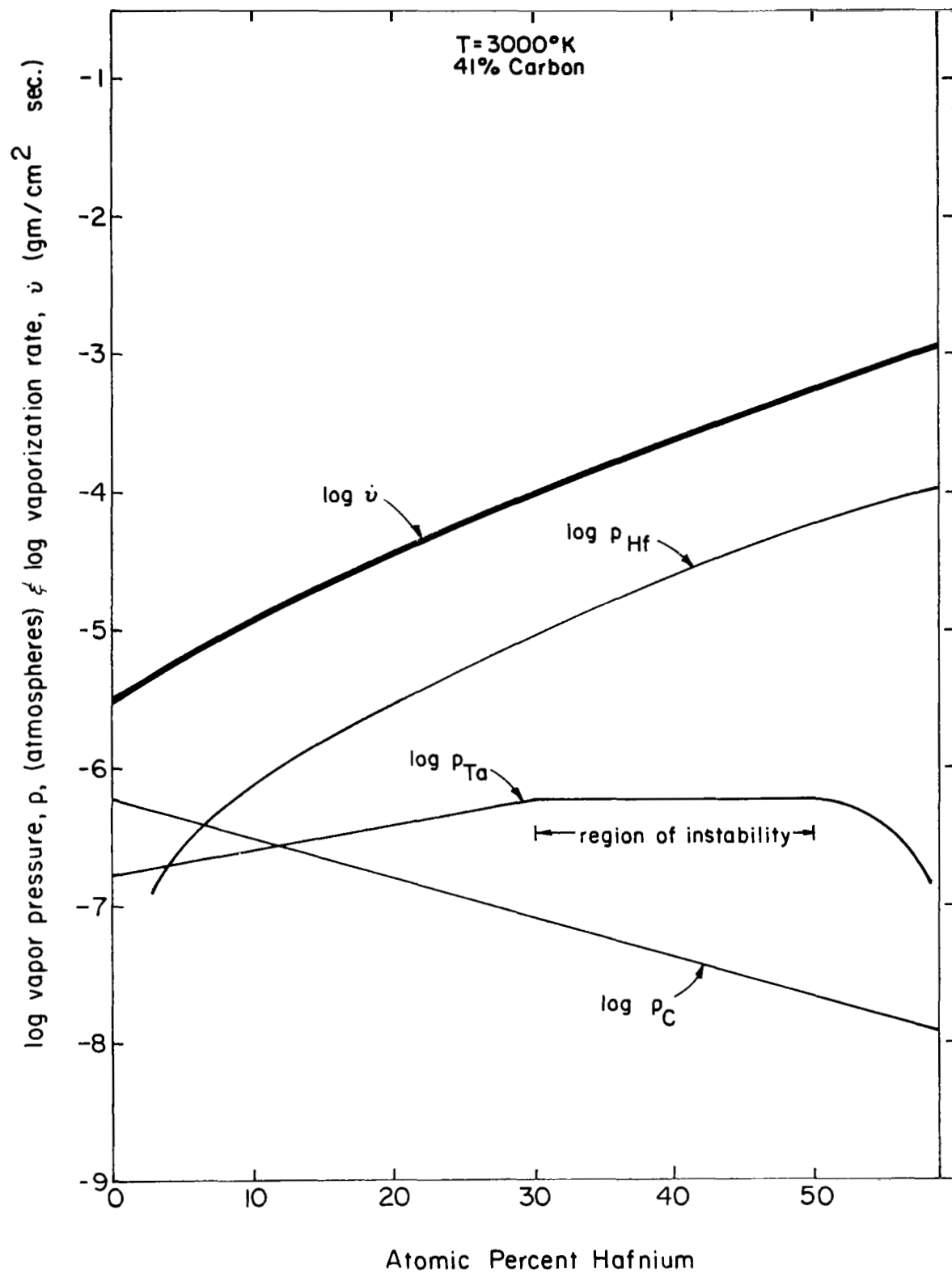
Fig. 15 - Vaporization of (Ta-Hf) C at 3000°K and 4

27

Fig. 16 - Vaporization of (Ta-Hf)C at 3000°K and 41% carbon.

28

The total rate of vaporization $\dot{v}$ has been computed by summation of the individual rates i.e.

$$\dot{v} = \dot{v}_{Ta} + \dot{v}_{Hf} + \dot{v}_{C} \tag{45}$$

Figs. (1-16) show $\dot{v}$ $[x, y, T]$ in addition to the individual pressures.

Reference to Figs. 1-16 shows that for most of the composition and temperature ranges explored, the vapor pressure of Ta is substantially less than Hf or C. Thus, all of the compositions will lose hafnium and carbon relative to tantalum. Consequently the real rates of vaporization should change with time reflecting changes in the composition. The computed values of $\dot{v}$ correspond to fixed compositions.

In the Hf-C binary, congruency phenomena are predicted and have been observed (see pp 21-38 of reference 2). These conditions correspond to unique cases where the rates of carbon and hafnium vaporization are such, that the ratio of carbon to hafnium atoms leaving the solid is the same as the ratio of carbon to hafnium atoms in the solid. This condition is represented explicitly by Eq. (46). *

$$(\dot{v}_{C} [x_{c}, y_{c}, T] / \dot{v}_{Hf} [x_{c}, y_{c}, T]) = y_{c}/x_{c} = \frac{p_{C}^{\sigma}[x_{c}, y_{c}, T] \, M_{Hf}^{1/2}}{p_{Hf}^{\sigma}[x_{c}, y_{c}, T] \, M_{C}^{1/2}} \tag{46}$$

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*In Eq. 46, the vaporization rates are in moles/cm^2 sec.

when $y = 1-x$, i.e. no tantalum is present, the establishment of congruency yields a stable composition. This situation is shown graphically in Figs. (10) and (11) of ref (2) and compared with experiment in Figs. (18) and (19) of ref (2). Thus the computed rate of vaporization for a congruency situation should be stable since the bulk composition does not change with time.

Since there are no such ternary congruency points indicated for Ta-Hf-C alloys (i.e. no solutions for Eq. (46) appear except when $y_c = 1-x_c$), it is expected that all of the compositions and rates of vaporization will be time dependent. However, it is possible to compute "quasi-congruency" conditions corresponding to situations where the ratio of Hf to C leaving the solid is in the same ratio as hafnium atoms to carbon atoms in the solid. This computation is performed by applying Eq. (46) to Eqs. 40 and 41 yielding.

$$2RT\ln(1-2y_c) = RT\ln p^o_C/p^o_{Hf} + 0.5 RT\ln M_{Hf}/M_C$$
$$+ F_{Hf+} + 3RT\ln\alpha - (1-x_c-y_c)(1-y_c)^{-1} 23,100$$
$$+ RT\ln 8(1-y_c)^2 \tag{47}$$

Eq. (47) can be employed by substituting various values for y_c, (i.e. $y_c = 1-x_c$, $y_c = 0.495$, $y_c = 0.49$, 0.48 etc.) and obtaining the corresponding values of x_c. These companion values of x_c and y_c can then be substituted into Eqs. 39 to 45 to compute $\mathscr{V}[x_c, y_c, T]$. Figs. 17 to 20 show the results of this computation.
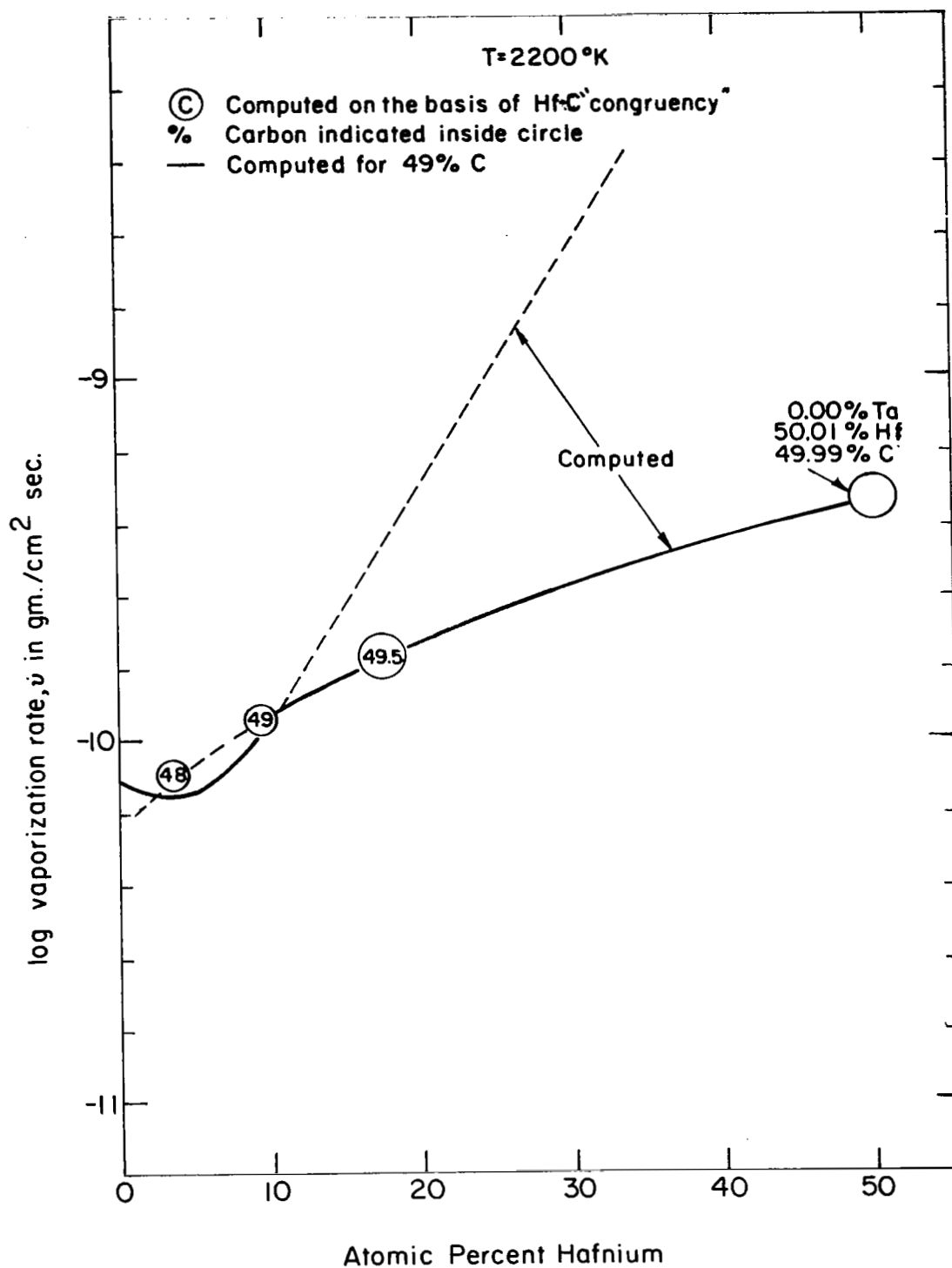
Computed initial rates of vaporization at 2200 °K.

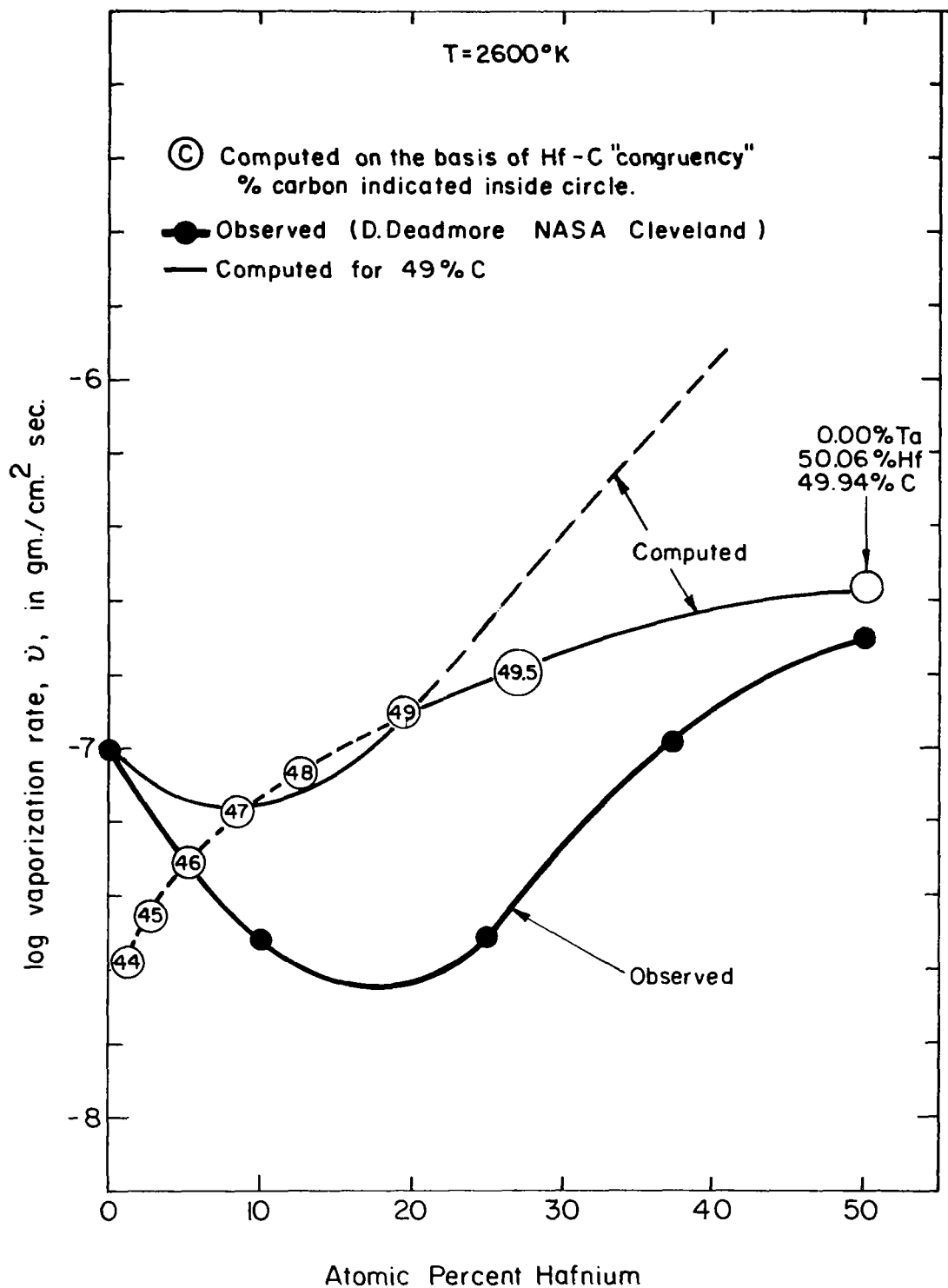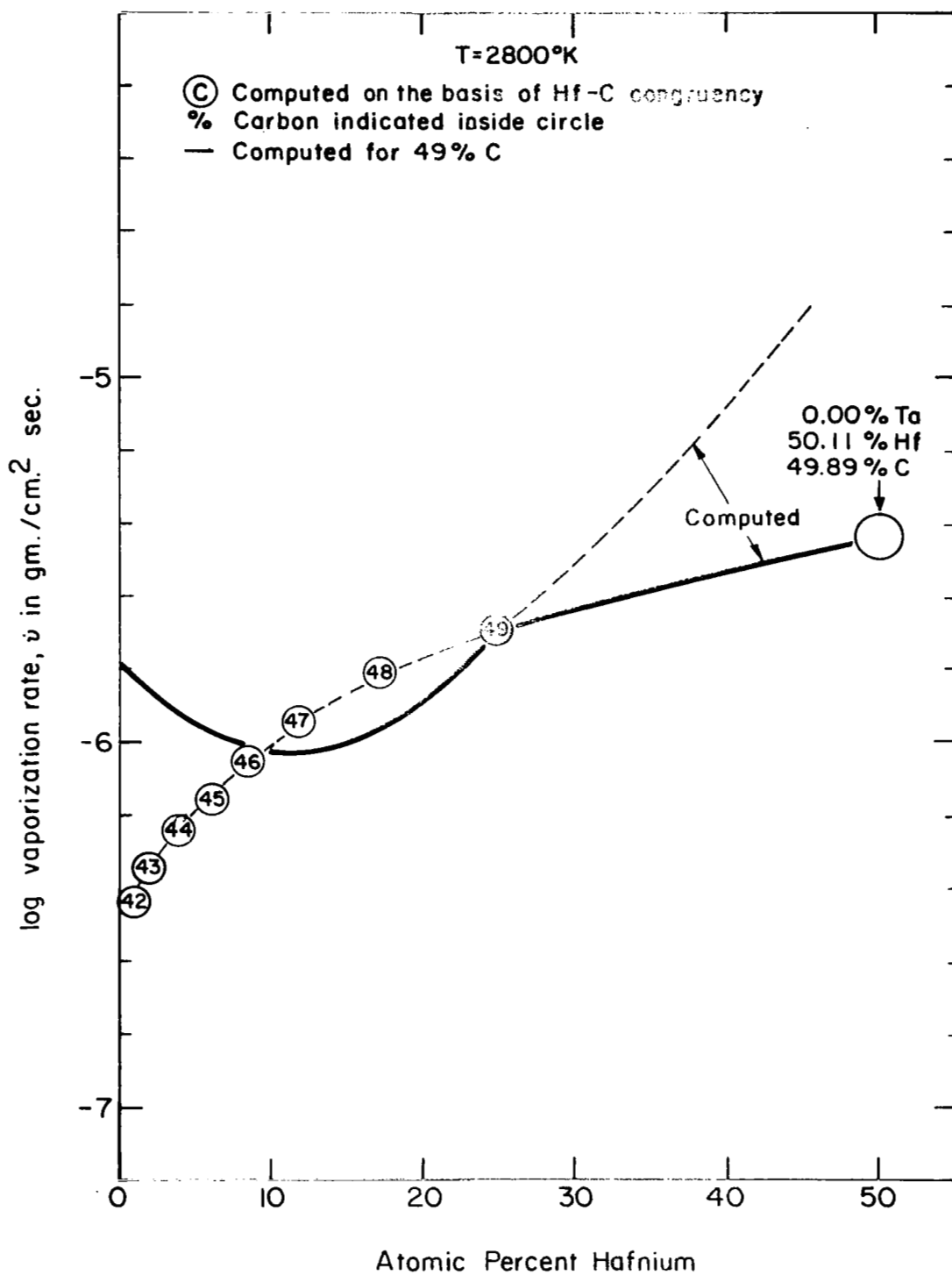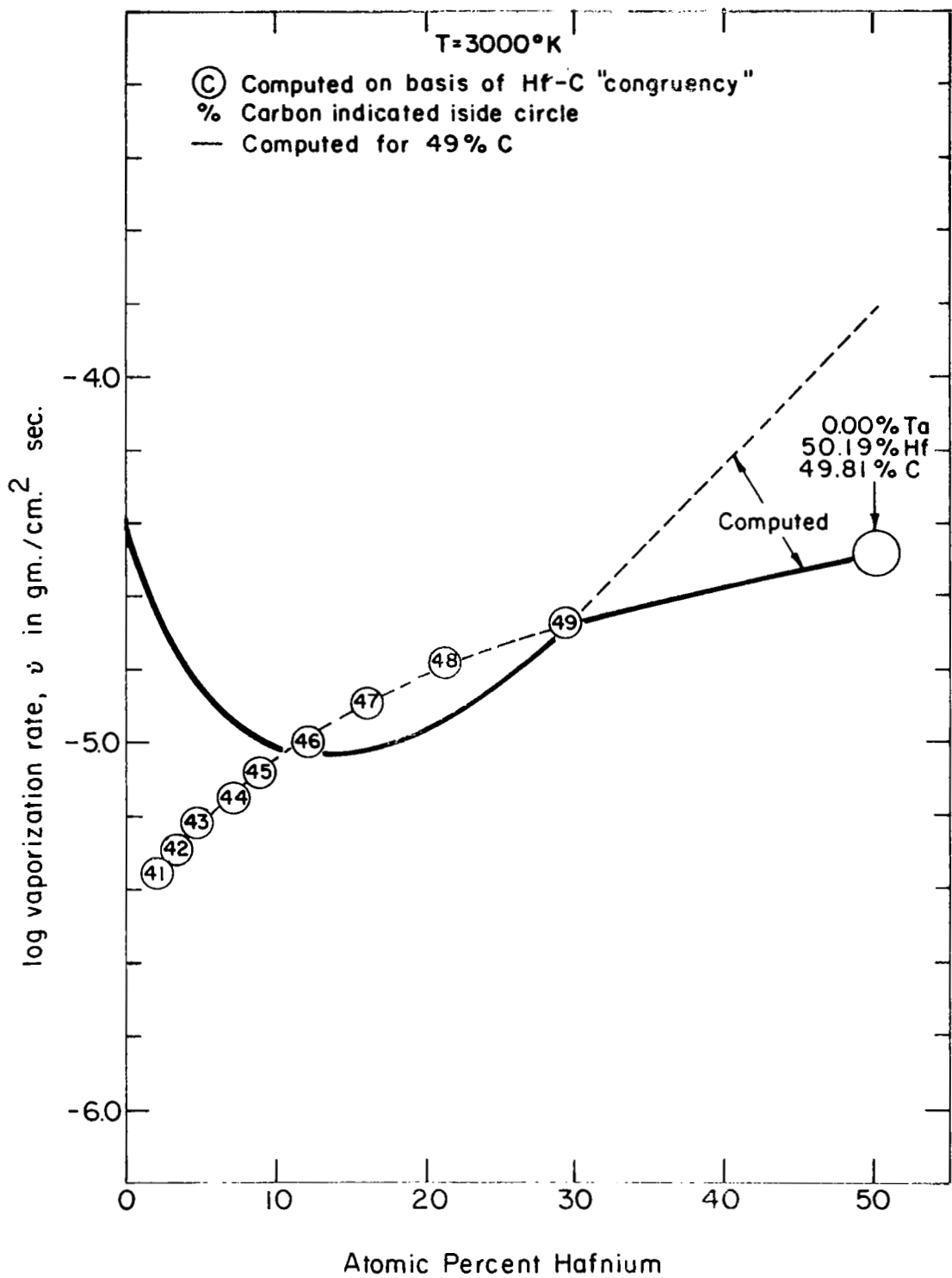Fig. 17 - Computed Initial Rates of Vaporization at 2200°K.

31

Fig. 18 - Comparison of observed (average) rates of vaporization with computed (initial) rates of vaporization at 2600°K.

Computed initial rate of vaporization at 2800°K.

Fig. 19 – Computed Initial Rates of Vaporization at 2800°K.

Computed initial rate of vaporization at 3000°K.

Fig. 20 - Computed Initial Rates of Vaporization at 3000°K.

34

In addition, Figs. 17 to 20 repeat the ϑ [x] curves corresponding to 49% carbon i.e. y = 0.49. The reason for including the 49% curves is as follows:

Fig. 18 corresponding to 2600°K shows the results of vaporization data obtained by Deadmore at NASA on a series of stoichiometric (50% carbon) Ta-Hf-C alloys at 2600°K. These data are the results of 2-4 hour exposures representing "average vaporization" rates. The Ta-C results at 2600°K yield $\vartheta = 10^{-7}$ gms/cm^2 sec. which corresponds to a carbon level of 49%. Reference to Fig. 21 (which is the companion to Figs. 14 and 15 of ref. 2) shows that if the experimental exposure time were extended, the carbon level should decrease resulting in a further reduction in ϑ. This reduction of ϑ is shown in Figs. 6-8. However, the exposure periods in the TaC case was only long enough to produce an "average ϑ" which corresponds to an "instantaneous ϑ" characteristic of a 49%C alloy. Consequently as a first approximation to the task of comparing the computed values of ϑ with those observed, 49%C is taken as a lower limit controlled by the exposure time. Thus we expect that the "quasi-congruency" ϑ corresponding to values of y_c equal to or greater than 0.49 can be reached and maintained, but that the exposure time required for reaching lower values of y_c is longer than the experimental exposure time.

On this basis the "computed" ϑ, x, y curve consists of two branches:

a) $\vartheta = \vartheta [y_c, x_c, T]$ for $y_c \geq 0.49$

b) $\vartheta = \vartheta [x, y = 0.49, T]$ for $y_c < 0.49$
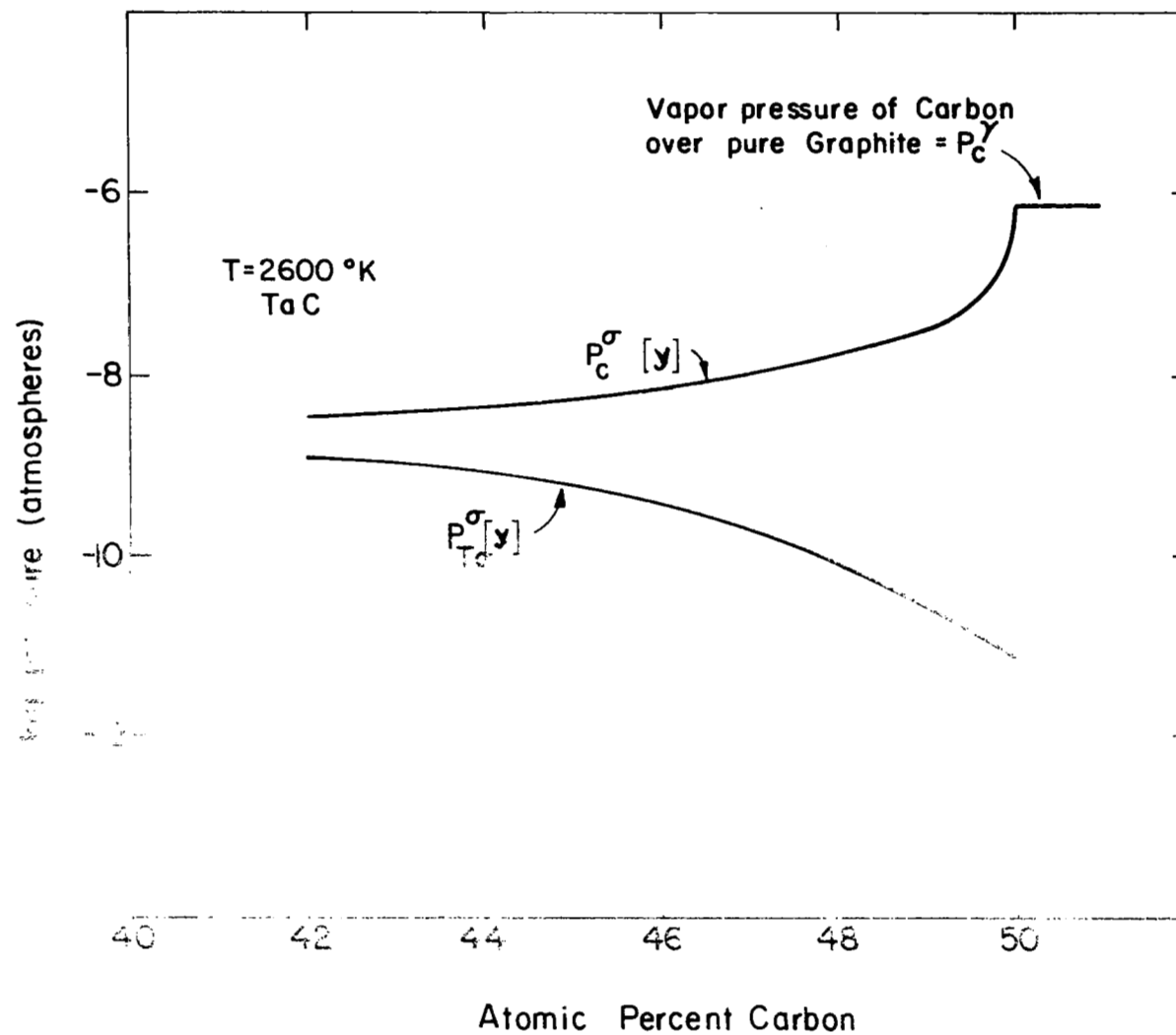
Fig. 21 - Calculated compositional dependence of the vapor pressures of Ta and C over the TaC$^{\sigma}$ phase at 2600 °K.

IV CONCLUSIONS

The Schottky-Wagner model of a two-sublattice compound has been applied to the (Ta-Hf)C ternary compound and detailed in a form which is sufficiently explicit to permit computation of the individual vapor pressures of the elemental components and the rates of Langmiur evaporation for a wide range of compositions and temperatures. As was pointed out at the end of Section III, the computed rates of vaporization represent initial or instantaneous rates corresponding to a fixed composition. The exception is pure HfC which exhibits congruent vaporization.

In view of the level of agreement between the predictions and available data (see Fig. 18) the thermodynamic description of this ternary compound detailed in Section III appears quite adequate. The comparison of predicted initial rates of vaporization and observed rates (Fig. 18) shows fair agreement, the maximum difference, being a factor of 5 at 2600°K. In addition, the appearance of a minimum in the rate of evaporation which is observed near 4TaC: HfC is also predicted by the present calculations. Under these circumstances the general agreement between the computed results and the experimental behavior appears quite satisfactory.

The present computations could be further improved by converting the equations for calculating initial rates of vaporization, Eqs. (42)-(44), to integrated rates of vaporization which might be compared with experimental data on a more realistic basis. The latter problem is an exercise in mathematics which does not require additional thermodynamic study.

For example consider a case similar to the binary Ta-C at 2600°K (Fig. 25) where the pressure of metal is lower than the pressure of carbon. If a composition corresponding to $y = 0.5$ ($x = 0$) is prepared, heated to 2600°K and allowed to vaporize, then the initial rates of vaporization $\dot{v}_C$ and $\dot{v}_{Ta}$ can be computed from Eqs. (35-44) as in Fig. (5). However, as the time of exposure increases from $t = 0$ to some finite time t, the composition will change. Since congruency conditions are absent, the specimen will loose carbon and y will decrease from the initial value, $y_o = 0.5$ at $t = 0$, to a value $y[t]$ which is less than 0.5. As this compositional change occurs, $\dot{v}_C[t = 0]$ will decrease (see Figs. 6, 7, 8).

In order to compute $\dot{v}_C[t]$ and $\dot{v}[t]$ for this case, the changes in composition must be taken into account. To illustrate the indicated procedure, consider a case similar to the TaC situation at 2600°K, i.e. $x = o$, where $y = 0.5$ at $t = 0$. Since the vapor pressure of tantalum is much lower than that of carbon initially, let us assume that $\dot{v}_{Ta}[t] \simeq 0$ as a first approximation. If w_C and w_{Ta} are the number of grams of carbon in the specimen then

$$y[t] = w_C[t] / (w_{Ta}^{\,o} M_C M_{Ta}^{-1} + w_C[t]) \tag{47}$$

where $w_{Ta}[t] = $ constant $= w_{Ta}^{\,o}$ and M_C and M_{Ta}^{-1} are the atomic weights of carbon and tantalum respectively; when $t = 0$, $y[t] = 0.5$. Eq. (44) defines

$$\dot{v}_C[y] = - \frac{dw_C[y]}{dt} = 44.4 M_C^{1/2} T^{-1/2} p_C[y] = y(1-2y)^{-1} K_C[T] \tag{48}$$

where

$$K_C[T] = 44.4 M_C^{1/2} T^{-1/2} p_C^{\,o} \exp[-F_{C+}/RT] \tag{49}$$

is constant at a given temperature. Substituting (48) into (47) yields

$$\frac{dw_C}{dt} = -K_C[T] \ (w_{Ta}^{\ o} \ M_C \ w_C^{-1} \ M_{Ta}^{-1} - 1) \tag{50}$$

Integrating yields

$$w_C - w_C^{\ o} = w_C^{\ o} \ \ln y/(1-y) + t K_C \tag{51}$$

hence

$$(1-2y)/(1-y) + \ln y/(1-y) = -t \ K_C/w_C^{\ o} \tag{52}$$

Eqs. (51) and (52) define $y[t]$ and the carbon weight loss (i.e. the total weight loss since dw_{Ta}/dT is assumed equal to zero) as a function of y and time. Combination of Eqs. (51) and (52) yields

$$-\frac{(w_C - w_C^{\ o})}{t} = \mathring{v}_C[t] = \frac{K_C \ (1-2y)/(1-y)}{(2y-1)/(1-y) + \ln (1-y)/y} \tag{54}$$

Eqs. 51 to 54 can be simplified by considering times short enough so that the $\ln(1-y)/y$ can be expanded in series approximation. This procedure yields

$$t \approx \frac{w_C^{\ o}}{2 K_C} \ \left(\frac{2y-1}{1-y}\right)^2 \tag{55}$$

and

$$\mathring{v}_C[t] \approx 2K_C \ (1-y) \ (1-2y)^{-1} \tag{56}$$

or

$$\mathring{v}_C[t] = (2w_C^{\ o} K_C/t)^{1/2} \tag{57}$$

Thus on the basis of the present simplified expression, the rate of evaporation is found to vary inversly as the square root of the time. A more complete solution of the problem would require relaxation of the assumption that $dw_{Ta}/dt = o$.

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40